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Fabian Fernandez-Luqueno
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Agricultural and Environmental Nanotechnology

Novel Technologies and their Ecological Impact

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Agricultural and Environmental Nanotechnology

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Preface

Agricultural and Environmental Nanotechnology: Novel Technologies and their Ecological Impact is an edited book comprising 24 chapters that highlights the best practices regarding nanoscience and nanotechnology for agriculture and environmental sectors to shape sustainable development thought to improve the quality and quantity of the agriculture products and to decrease the collateral effect of nanotechnology in the ecosystems. Besides, leading nanotechnologies are shown and discussed to guarantee their proper management in lands and ecosystems. Therefore, nanotechnologies such as agro-nanobiotechnology, nanofertilization, pest control, magnetofection for plant breeding, plant molecular farming, OMICs technologies, phytonanotechnology, nanoremediation, etc. are described in 5 different parts and 24 chapters. Undoubtedly it is an ideal and updated book for undergraduate or postgraduate students, and scientists or researchers involved in nanoscience, nanotechnology, crop production, and remediation technologies as well as for those researchers solving technical problems regarding crop management and human and environmental health without hampering the pursuit of sustainable development goals.

We are grateful to the authors of this book, who helped to bring this volume to light. We wish to thank Dr. Emmy Lee, Associate Editor, Springer Nature Korea Limited, for her generous assistance and persistence in finalizing the edited volume. Special thanks are due to our esteemed colleagues and university authorities for their kind support and constant encouragement throughout the task. Finally, specific thanks go to our families and friends for their support and cooperation in putting everything together.

Ramos Arizpe, Mexico — Fabián Fernández-Luqueño
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About the Book

Agricultural and Environmental Nanotechnology: Novel Technologies and Their Ecological Impact is an edited book consisting of 24 chapters written by eminent experts from around the world on recent advances in the field of agricultural and environmental nanobiotechnology. This book highlights the best practices regarding nanoscience and nanotechnology for agriculture and environmental sectors to shape sustainable development thought to improve the quality and quantity of the agriculture products and to decrease the collateral effect of nanotechnology in the ecosystems. The book will be helpful for professionals, researchers, and scholars working in the field of agricultural and environmental biotechnology in particular.

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Nanoagriculture: Advantages and Drawbacks

Sarita Yadav, Neha Sawarni, Twinkle Dahiya, J S Rana, Minakshi Sharma, and Bhawna Batra

1 Introduction

Nanotechnology is derived from "Nanotech," a study of manipulating matter on atomic and molecular scale (Arivalagan et al. 2011). In present days, nanotechniques have achieved great attentions because of its various roles in many fields such as energy storage devices, clinical drugs, catalytic process, and materials (Fig. 1). Several reports also revealed that nanotechnology would have a major and prolonged effect on the agriculture sector. Agriculture is an ecologically costly technique (Ghidan and Antary 2020). An increasing number of peoples and unfavorable climatic situations increase the requirement of using pesticides and chemical fertilizers. However, they tend to have high adverse effects as they release toxic molecules in high quantity in the environment. The main solution of this issue is formation of nanomaterials-based fertilizers and pesticides. These can also help in decreasing the wastes. By using nanotechniques, agriculture is developing fast (Editorial Board 2020). Nanotechnology emerges as a boon to agriculture with new tools and techniques to increase crop production sustainably and protect crops from pests (Marchiol 2018). There are several roles of nanotechnology in the area of agriculture like rise in production rate by using nanofertilizers and nanopesticides, enhancement of the plant growth by employing nanomaterials (like carbon nanotubes, titanium dioxide, and silicon dioxide), increase in quality of the soil by

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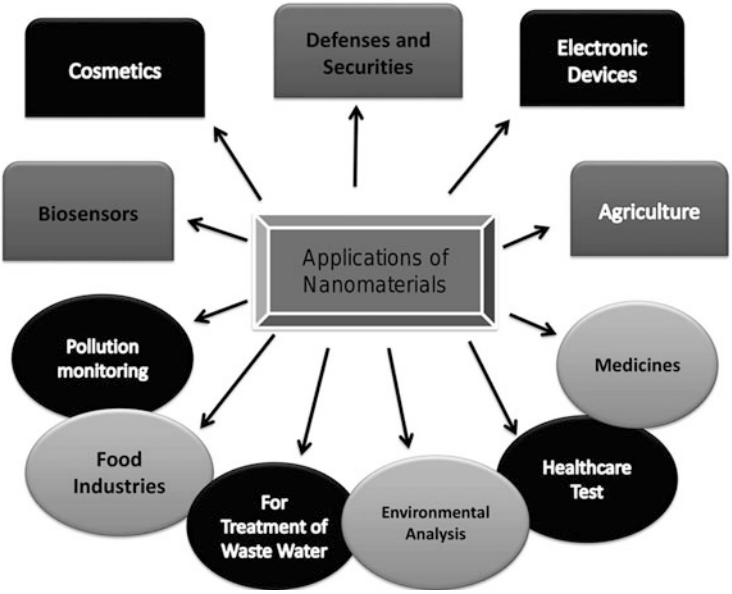

Fig. 1 Applications of nanomaterials in various fields

using hydrogels and nanofertilizers, and give better survey by employing wireless nanosensor tools.

Moreover, these techniques help to control the discharge of toxic substances from agrochemicals (like fertilizers and pesticides) and deliver many needed macromolecules on desired sites to improve the disease resistance of plants (Fraceto et al. 2016). Origin of nanosystems like nanobiosensors, nanopesticides, and nanofertilizers, surrounded by different plants to enhance solubility, amplify bioavailability, advance targeted delivery and control release over generation, will extremely advance the agricultural value chain. Hence, nanotechnology in the field of agriculture will upgrade the systematic measure of fertilizers, enhance management of pests and vectors, lessen chemical pollution and eventually reduce exposure with agriculture operators (Phenny 2018). Over the last few years, nanomaterials are considered as a substitution for plant pests' control which consists of weeds, insects and fungi. In addition to all these perks, a large number of nanoparticles like TiO2, Cu, Al_2O_3, Ag, Si, CeO2, Al, Fe, ZnO, Zn, and nanotubes of carbon are announced to have few negative impacts on yield of crop plants, soil microbes, enzymatic activity of soil and on nutrient cycle aside of all antimicrobial properties (Ghidan and Antary 2020).

2 Advantages of Nanotechnology in Agriculture

A few main advantages of nanotechnology in the area of agricultural research are as following: Nanogenetically, rise in crop production rate, agriculture monitoring, delivery of drugs, nanofertilizers and their slow release, nanoherbicides-nanopesticides, Nanomaterials as priming agent (Nanopriming), in recycling agricultural waste, in agriculture machinery, and Nanobionics in photosynthesis (Fig. 2).

2.1 Nanogentically Rise in Crop Production Rate

A new set of tools are provided by nanobiotechnology to handle the genes by nanoparticles, nanofibers, and nanocapsules (Agrawal and Rathore 2014). Scientists said that nanotechnology is moving toward uplifting the agricultural genetic engineering to one step ahead to atomic engineering. Seed's DNA can also be re-sequenced in a way to get various properties of plants like color, season of growth, and production (Singh and Prasad 2017). In the process of delivering drug, crop engineering and environmental regulating nanofiber array with prospects implementation can give genetic material to cells fast and effectively. Combination of nanofibers of carbon that are changed via DNA of plasmid gave a regulated biochemical change in cells (Singh and Prasad 2017). Purity of genes can be checked

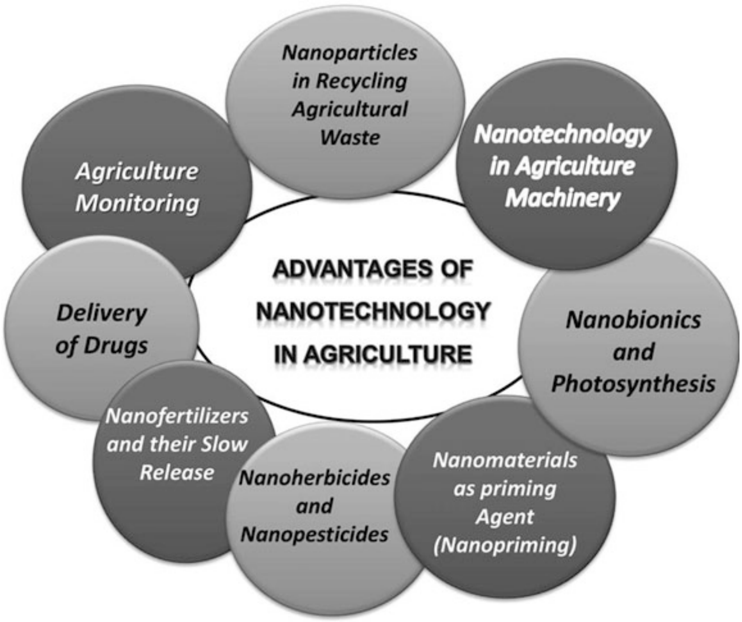

Fig. 2 Advantages of nanotechnology in agricultural area

by watching load of pollen grains that surely cause pollution. Bio-nanosensors are used to give a check on pollution and also help to reduce contamination. It is specific to pollen pollutants. To reduce mixing of pollen into a pollutant, crop field from genetically modified crop bio-nanosensors are used. Nanobarcodes which are durable, encodable, and machine-readable and submicron-sized taggants are used to detect original genes which are combined with seed and vend in retail. Seeds are the main source to spread various illnesses in plants, and most of the time pathogens are responsible to damage stored seeds. Mn, Pt, Ag, Zn, Pa, Au elements are used in nanocoating of seeds that help to decrease the demand for elements and also save seeds. Su et al. developed a technique called quantum dots (QDs) that is used to differentiate unviable and diseased seeds. It acts as a fluorescent marker (Agrawal and Rathore 2014). Smart seeds are those seeds which are consumed with nano-encapsulated strain of bacteria which are used to decrease rate of seeds, enhance crop yield, and give an accurate field stand. For reforestation and germination during good moisture availability, smart seeds could move over high range of mountains. Seeds covered with nano-membranes permit to check the present amount of water to seeds to chunk right time for germination. To decrease the level of damage, seeds implanted with the particles of magnetic properties are used to find the moisture content at the time of seed storage. Nowadays to estimate age of the seed, bio analytical nanosensors are used as they are upcoming driven areas of research (Rawat et al. 2018). Functional nanomaterials act as transporter and can carry huge no of genes and other substances that are used to stimulate expression of gene and also give a check on liberation of genetic material every time in plant body. To distribute non-stop DNA into complete plant cell, these days gene gun or particle bombardment is used. Bombardment particles are made up of gold as it is nonpoisonous to cell and quickly adsorb DNA. The vital benefit is to distribute all the effecter molecules and DNA to their targeted places at same time and also show expression of chemicals and genes (Nair et al. 2010).

Chitosan nanoparticles are adaptable; however, their transfection productivity could be changed, and they could be PEGylated in sequence to manage liberation of genetic materials as the time passes. The implementation of starch nanoparticles, which are fluorescently labeled, behave as transgenic carriers in plants. These designed nanoparticles, which are basically biomaterials, are in a way that they can attach and carry forward genes to the cell wall of plant cell. By the help of ultrasound, it stimulates pore channel in nuclear membrane, cell wall, and cell membrane. Silver nanoparticles (SNPs are covered with plasmid) which are covered by DNA treatments found to stimulate petunia's isolated protoplasm and transfer DNA in plasmatic form to the nucleus of the cell via ethylene glycol with incubation process (Ammar 2018). In the era of nanotechnology, nanoparticles have an exclusive characteristic that plays a significant role in photosynthesis and in improving crop yield. In nanoagriculture, an insight to the basic interrelationship between nanoparticles and plants is necessary for long-term advancement. As there is a belief that nanoparticles play a vital role in providing more sustainable agriculture. Previously, some studies were carried out by using protoplast of mesophyll cells which retains same biological response and cellular activity as integral plant. Therefore, these were further adopted as a prototype to check the effect of nanoparticles on photosynthesis. The protoplasts of mesophyll cells were separated from spinach and cultured with various metal ions like Fe, Mn_3O_4, SiO_2, Ag and MoS_2, dosing with an amount of 50 mg/L for 2 h under light. Crop yield and ATP generation of protoplasts were efficiently enhanced to 23% by using Mn_3O_4 and Fe nanoparticles and were reduced to 43% by using Ag and MoS_2 nanoparticles. Furthermore, the enhanced effect of Mn_3O_4 and Fe nanoparticles was monitored by photo-electrochemical studies in terms of current and rate of electron transfer. GC-MS-based technique results were suggested that Fe and MoS_2 nanoparticles changed the metabolic profiles of mesophilic cells at the time of 2 h of light period. Partially, exposing the impact of nanoparticles on photosynthesis and biomass has been implemented over whole plant. The findings suggest that a stable reciprocity with protoplasts database showed enhanced biomass on exposure with might be a rapid Mn_3O_4 (57%) and was reduced by 24% on specific treatment with silver nanoparticles. Hence these findings reveal that protoplasts might be a rapid and valid tool for screening nanoparticles to increase the rate of photosynthesis for efficient use of nitrogen-fertilizer system (Wang et al. 2020).

2.2 *Nanosensing Techniques and Agriculture Monitoring*

Nanosensors nowadays can be used as regulator and system of control foe CEA (controlled environment agriculture) to give rapid management to take a decision on crop lifetime, issues related to food security (microbial and chemical pollution) and best time for harvesting (Shukla et al. 2019). Nanobiosensors consist of small-sized substances which behave as bioreceptor on a transducer that gave signal to identify element to check single/multiplex analyte (Arduini et al. 2016). The implementation comprises observations of analytes; for example, proteins, urea, hormones, pesticides, and enzymes are used to detect metabolites of many pathogens and microorganisms (Agrawal and Rathore 2014).

Following are the types of nanosensors:

1. Physical: The characteristics of nanotubes or nanoribbons get deformed due to some changes, for example, variation in voltage occurs due to change in pipe.
2. Chemicals: Principle of its operation depends on the characteristics base on electronics of nanotubes and nanoribbons get deformed because of absorption of various molecules. Threshold voltage can be deformed due to the availability of various molecules.
3. Mechanical: Scale of mechanical measurement is level, distance, movement, and position.
4. Biological: Bioreceptors are present here. This biological system consists of any form of DNA, protein, antibody, enzyme and also a transducer like that optical or magnetic checker (Alvarado et al. 2017).

3 Characteristics for Ideal Nanobiosensors

Nanobiosensors are very much particular for analyte it means that the sensor is capable to differentiate in between different matter and analyte.

- Physical measurements like temperature, stirring, and pH are independent to the communication of analyte.
- Duration of reaction must be less for proper working.
- The response produced by analyte must be away from electrical noise, exact, linear specific and reproducible.
- Properties of nanobiosensors must consist of following characters like their size must be small; they must be non-antigenic, biocompatible and must be non-toxin in nature.
- For everyone benefits they should be less in cost, movable and are also able to operate by semi-skilled operator (Rai et al. 2012).

Nanobiosensors gives the merit to exist as tiny, movable, sensitive, along with real time recording, accurate, significant, good, exact, consistent, vigorous and steady that can conquer the deficiency of present sensors. Nanobiosensors machinery can boost in prior apprehension and quick conclusion to amplify crop production by satisfactory regulation of pesticides, land, fertilizers and water (Scognamiglio 2013). Controlled Environmental Agriculture (CEA) might be refined by usage of nanosensors are increasing the ability to regulate the schedule of crop harvest, reveal crop health and regulate chemical and microbial impurities of crop. Precocious nanosensors had been reinforce that may be connected to GPS technique and build real time observation of crop husbandry encouraging by settling autonomous biosensors (Agrawal and Rathore 2014). Prior finding of soil toxins can assist to keep away their adverse effects. Due to collection of definitely poisonous metal ions in production soils and plants more than doorway levels is a general issue with concern to major health threat (Gruber et al. 2017). Intense farming show environmental contamination and unsustainable agriculture practices which ultimately leads to destruction of useful resources like water and land. These situations are now days enhanced due to high population of world and due to a huge climate change is also responsible for all of this. Nanostructured biosensors are act as a leading technology that can control these problems. As we all know this, biosensors based on nanotechnology are basically useful to give exact, cost efficient, quick response in analysis to field like plant pathogens, soil humidity, water and soil pesticides. They are exploiting the characteristics of functional material which give amazing properties at nanoscaling (Antonacci et al. 2018).

Many biosensors for example optical biosensor, ssDNA-CNTs probes are used to find types of DNA oligonucleotides, a modified GCE which is a film composite of MWNT/ZnO/CHIT is used to immobilized ssDNA probes for efficient differentiation of various DNA series. To detect deep DNA damage, in chiton nanobiosensor along with bionanocomposite layer of MWNT get added to SPCE. GNPs containing nanobiosensors get worked with alkanethiol capped DNA/LNA via tail to tail mode of hybridization basically for ssDNA. Label free EIS is used to detect PAT gene series via nano-SiO_2/P-aminothiophenol (PATP) sheet. Maki et al. stated that which depends on nanowire field efficient transistor get very sensitive and also help in find in g the ultra-sensitive electronic DNA methylation. By using this PCR amplified and difficult bisulfate treatment can be inhibited (Marchiol 2018; Usman et al. 2020). Finding of unique protein molecules is completely depend upon biosensors which are depend upon biosensors that are dependent on protein-nanoparticles by using interaction ability of ligand-protein. Problems related to decreased mineral level in plant body, plant pathogens, differentiation of one plant species to other one and biomarkers can easily find by DNA-protein biosensors (Rai et al. 2012).

Moisture and temperature of soil is vitally important in field of agriculture. Watering regulation should come by with exact refurbish about soil moisture at the root level of plants. Wireless nanotechnology-based sensors with water sensitive nanopolymer coating are comprised of micro machined MEMS (micro electro mechanical system) for moisture detection and also find temperature variation on chip piezo resistive temperature sensor. With the help of microelectronic circuits the sensors have the ability to regulate and record temperature and moisture (Usman et al. 2020). To regulate soil moisture updates few fresh matters with upgraded characteristics of quick response, stability, accessibility; sensitivity particles with nano size structure are used. Ag/Pd combined electrodes and oxide films of grapheme are few example of ceramic substrate coated nanobiosensors with wide range response and sensitivity. With the help of ion transport and graphene oxide films dispersion concentrations these sensors utilize the properties of ceramic substance and NMs (Usman et al. 2020). Nanonetworks for regulating conditions of plant may change spontaneously indicating more systematic usage of crop inputs (e.g., pesticides, fertilizers, and water). The real time and observation of crop growth guides to exact and in time decisions, less cost and waste and it enhanced quality production (Marchiol 2018). For crop production urea is the most commonly used fertilizers and source of urease, nitrate and nitrite which are universal pollutant in water leading eutrophication causing surrounding implication. Impurities based on calorimetric assay and microfluidic impedimetric in water and soil is detected by nanobiosensors (Mura et al. 2015; Delgadillo-Vargas et al. 2016). In electronic noses (e-noses) considered as biosensors of next generation and artificial intelligent system, nanotechnology is used. To evaluate plant diseases insect infestation and soil/water impurities and to regulate production processes, nanotechnology has been frequently used in agriculture (Hu et al. 2019).

3.1 Nanotechnology in Delivery of Drugs

A wide range of chemical checking and settlement potential regarding self-regulation can be served by nanoscale which acts as carrier. Exact amount of nutrients, medicines and other chemicals required for agriculture can be distributed by these quick techniques. To regulate or decrease the utility of antibiotics and pesticides, these sharp techniques are used (Sharon et al. 2010). Few nanoparticles which are the small forms of various elements like silica, carbon, aluminum-silicates, and silver are used to control illness of plants. To enhance illness and stress resistance, silicon acts as the best absorbent for plants which enhance the development of physiological activity of plant. Downy mildew and powdery mildew occur due to microorganisms which are pathogenic in nature can be easily prevented by solution of aqueous silicates. Increased activity of antimicrobes can be attained by silver in its ionic form. Due to its more reactivity and the power to reduce and oxidize readily into metal, silver is highly unstable; because of this property it could not attain antimicrobial activity regularly. By another side, silica has no straight outcome on microorganisms which are pathogenic in nature and no reaction on illness. So to control many plant illnesses new small sized silver-silica composition has been developed (Sharon et al. 2010). Antifungal working of both nanoparticles on *Bipolaris sorokiniana* and *Magnaporthe grisea* assessed by in vitro and in vivo methods exhibited reduced disease development by phytopathogenic fungi. By controlling cellular functions of Botrytis cinerea, nanoparticles of zinc oxide hindered their fungal growth that leads to distortion in mycelium mats. Growth of conidia of penicillium expansum and conidiophores is hindered by zinc oxide nanoparticles that at last cause death of fungal mats as stated by Abd-elsalam (Abd-elsalam 2013). To boost up nature fibers example coconuts (*Cocos nucifera*) sisal (*Agave sisalana*), carbon nanofibers are used (Misra et al. 2013).

3.2 Nanotechnology in Delivery of Drugs

In various research fields, nanotechnology has a great advancement in transportation and delivering of drugs or any other agents. Meanwhile, in the field of agriculture, factors related to productivity of crops have raised concerns about their ability to upgrade; higher affinity and viability depicted a major challenge. In (Mura et al. 2015) author developed nano-vectors produced through lipids from olive pomace, a substance exists in form of waste in oil processing with the purpose of enhancing the efficacy of latest synthesized transporters/carriers. Researchers were proposed lipid-based nano-formulations to administered the phytohormones to various strains of *Olea europaea*, which enabled cost-efficiency and ecologically sustainable processes. However, it has been also studied that for implementation, adjuvants, also known as natural lipids formed a stable and well-organized nano-objects were used. In vitro and in vivo studies revealed that rooting has been increased in respect of traditional treatments, because of that it has been represented that the fabrication of novel nano-formulations had remarkable effectiveness for comprehensive administration of chemicals in terms of endurable economy in agriculture field (Mura et al. 2015). Nowadays, durable and eco-friendly agriculture farming has growing interest towards nano-vectors as they have an effective impact on plants growth. These nano-vectors have biomedical and industrial application too. Hence, novel and advanced processes have been used for plant growth with the help of appropriate nanomaterials. The main objective was focused on newly synthesized polymeric nano-capsules which further utilized as bio-compatibility nano-vectors for transportation of bio-active mixtures to plants. Moreover, nanoparticles have been synthesized as from a waste material; lignin, which is the derived product of wood processing. Precisely, they were loaded lignin nanocapsules with gibberellic acid (GA) and evaluated in reproducible manner that nanoparticles might be achieved in a range of 0.5–1.5 mg/mL GA content, that is, significant for transportation targets. Bare and GA nanocapsules were specifically characterized by DLS and SEM techniques. In vivo and in vitro cyto-toxicological assays and release of cargo were performed in two standard plants *Eruca vesicaria and Solanum lycopersicum* to study the proportion of germination, stem and primary roots along with basic physiological conditions of treated and un-treated plants. Additionally, nanocapsules were applied with lipid staining solution to follow their access and aggregation in seeds and sprouts (Clemente et al. 2018). Prolonged release and smart drug delivery of agro-chemicals are essential for implementation of dynamic crop protection with least damage to the ecosystem. Previously work has been done for effective crop protection, which reveals a novel and less expensive approach to construct ligno-cellulose- based bio-degradable porous matrices as they were able to constant release of loaded molecules. The matrix reveals adjustable physiological and chemical properties on conjugation with wrap-and-plant concept, which initially helps in utilizing as a defense mechanism against soil pests at the time of prolonged release of crop protection fractions. The prepared matrix was produced by mechanical treatment of the ligno-cellulose fibers derived from banana plants and their impact of various extents on the crop protection was also monitored. Alteration in structure, composition of fibers and mechanical treatment had a great influence on morphology, efficiency and porous nature of matrices. To authenticate this hypothesis, the impact of morphological and lignin content ratio modified the release of rhodamine B and abamectin as model cargos was analyzed. Therefore, banana-fibrous sources revealed a remarkable release profile of the matrices and will be selected for crop protection contrary to non-banana fibrous sources (Hu et al. 2019).

At present time, food security is the leading universal concern due to plenty of problems like biotic–abiotic stress factors and global warming which commonly leads to reduction in agricultural land. Therefore, a unique solution has to be prepared to overcome this major challenge without excessive use of pesticides and fertilizers. In recent years, the advancing and improvement in gene-editing technique were found very crucial. With the use of gene-editing technology, scientists may targeted the particular genes and transform plant genomes to increase crop production at various levels. Nanotechnology with gene editing developed an integrated approach which is beneficial for plant bioengineering. Moreover, this chapter focuses on smart nanosensing platform which includes functionalized 2D-nanomaterial, MWCNTs, AuNPs, and quantum dots for specific gene delivery to the host plant cells and their functionality with the help CRISPR gene system. Still the process of absorption of nanoparticles in plants were not exactly recognized, hence the feasible endocytosis mechanisms were remains in controversy. Nanosensing provides a platform for inorganic smart nanoparticles which will produce advanced concoctions at the level of molecular breeding in plants and encountered as a latest carrier for the direct insertion of CRISPR gene as gene editing systems in different plant cells (Mostafa et al. 2021). Nanovectors based on lipid content were also providing a platform for transportation in several fields. Although these nanovectors have excellent biocompatibility but recently it raised concerns about their process of sustainable development in researchers mind. Especially, in case of agro-nanoscience where an extensively massive production has been required, becomes a challenging issue. For this reason, author in (Clemente et al. 2019) suggested green synthesis of novel nano-formulations for specific delivery of phytohormones (indole-3-butyricacid and 1-naphthaleneacetic acid) to *Olea europaea* L., achieved through waste extracted from the plant by their own, gained favorable outcomes on engineering pure form of phospholipids in little aliquots. They were utilized cryo-TEM, X-ray and neutron scattering technique for evaluation of data. All outcomes were found compatible and very consistent; demonstrating the efficacy of the applied auxiliary phospholipids imposing the fundamental configuration (Clemente et al. 2019).

3.3 Nanofertilizers and Their Slow Release

Huge enhancement in crop production more likely in cereals gave a remarkable role to meet nutritional requirements of whole world by last five decades. To enhance crop production more usage of chemical fertilizers plays a major role in this aspect. Utility of chemical fertilizers has been multiplied due to fertilizer-responsive crop diversities. Due to poor use, effect of fertilizers is somehow limited, fertilizers (by volatilization and leaching) that pollute the surrounding and enhance the cost of productivity that leads to poor use of chemical fertilizers (FAO 2017). Take an example, in standard fertilizers, 50–70% of nitrogen is applied that is lost to the surrounding (DeRosa et al. 2010). In these circumstances, to improve availability of less available nutrients, to decline the loss of mobile nutrients, and to promote slow release fertilizers, nanotechnology is used. Nanomaterials which are called nanofertilizers are either behaves as transporter/additive (by mineral compositing) or nutrients (micronutrient or macronutrient) themselves (FAO 2017). By summing up all the nutrients within the nanomaterials can easily form nanofertilizers (DeRosa et al. 2010). Soluble fertilizers get an eminent opportunity of choosing slow-release fertilizers as during the crop expansion nutrients are liberated at slow rate. Nanomembrane binding coating on fertilizers particles ease slow and steady deliverance of nutrients example apparent nanocomposites having K, N, P micronutrients, mannose and amino acid which boost up intake and usage of nutrients by grain crop as stated (DeRosa et al. 2010). Linkage to enhanced yield rate (by 32%) and growth rate (by 20%) of soyabean (*Glycine max* L.) is due to enforcement of nanofertilizers. This enhanced yielding comparison is done with those which are treated with those which are treated with conventional fertilizers (Kah et al. 2018).Due to lack of proper knowledge of using zinc nanoparticles to strengthen the inadequate soil with zinc validate various analysis studies with a possibility of better efficacy of zinc based nanoparticles for better crop yield and overall growth of the plant. The effect of efficacy of zinc based nanoparticles were examined on seed generation in soyabean (*Glycine max* cv. Kowsar) at a lifespan of 120 days, centering on morphological conditions and depends on the level of concentration of biomarkers for antioxidant defense system. This objective were performed through an analytical devise strategy that has become possible for researchers to develop three different zinc based nanoparticles of different shapes and sizes such as spherical, floral and rod-shaped having 38nm, 59nm, >500nm size respectively. Each nanoparticles were exists with higher sterility, crystal lattice, and negatively charged surface area; and also cross-checked with zinc ions to check the toxicity. Particular pot had two seeds, grafted with soil and N_2-fixative bacterium (*Rhizobium japonicum*), and matured in nature for a time period of 120 days. The outcomes were revealed a great impact of zinc-based nanoparticles on crop yield, oxidative degradation of lipids, and several bio-marker based supplement in soybean. Spherical zinc-oxide nanoparticles were better protected contrary to the floral-shaped nanoparticles, rod-shaped nanoparticle and zinc ions, specifically fewer than 160 mg zinc per kilogram. Despite that, in soyabean spherical zinc-oxide nanoparticles were triggered the highest aerobic stress response contrary to other two structurally distinct zinc-oxide nanoparticles when tested on the higher amount of 400 mg zinc per kilogram. Evaluation of all endpoints determined that the concentration-response curves for the 3 types of zinc-oxide nanoparticles and zinc ions were existed in non-linear manner. Overall evidences indicated a differential eco-toxicity of zinc-oxide nanoparticles in contrast to toxic nature of zinc ions in soybean. Highest level of no- to notice-harmful-consequences-level of 160 mg zinc per kilogram has been demonstrated that the efficiency for using zinc-oxide nanoparticles as a modern and powerful nanofertilizer for crops developed in a region of scarcity of zinc in soil to upgrade crop yield, quality of food, health and nutrition, all over the world (Yusefi-Tanha et al. 2020). Intake of nutrients and plant metabolism is improved via pores of nanometric regulated by nanostructure cuticle pores or molecular transporters are improved by metabolism of plants (Rico et al. 2011).

According to source, use of titanium oxide (TiO_2) on food crops leads to enhance growth of plant by 30% decreases intensity of diseases, enhanced photosynthetic rate. Use of TiO_2 leads to give eminent productivity in Oliver cereal like maize by decreasing the outcome of Curvularia leaf spot and occurrence of serious leaf blight diseases. Some reports stated that usage of TiO_2 remarkably decrease the productivity of rice blast and tomato spray mold along with nearby 20% enhancement in weight of grain because of yield regulated outcome of TiO_2 nanoparticles (Agrawal and Rathore 2014). Titanium dioxide, aluminum and silica combination was stated to be most influencing in power to control downy and powdery mildew of grapes via acting directly on interposing with identification of plant surface and boost up physiological defense of plant (Cacique et al. 2013). Allotropes of carbon with cylindrical structure include carbon nanotubes (CNT) are used as a carrier to transport required molecules that might be nutrients or biocides present in seed during the process of germination. By hydrolysis either in acidic or neutral medium, triazophos can significantly protected by taking it in a nanoemulsion form (Gutiérrez et al. 2011).

As founded by Ghormade et al., an essential oil from *Artemisia arborescens* comes under some difficulties regarding the stability at the time of action that is hostile to Aphis gossipy young and adult *Bemisia tabaci* and *Lymantria dispar* (cork plant pest). Addition to *A. arborescens* essential oil in solid lipid form nanoparticles that decrease the fast evaporation of essential oil when compared to referred emulsions. In the same way, essential oils extracted from garlic when get onto a polymer. NPs (240 nm) designed by polyethylene glycol (PEG) for the calculation of their insecticidal action against adult *Tribolium castaneum* that give somehow higher than 80% efficiency after 5 months, in case to regulate steady liberation of active components when compare to free essential oil if garlic (11%) (Agrawal and Rathore 2014).With the rise of population, nurture nutrition security of individuals had been a tremendous challenge. Researchers have addressed several approaches to sustain food for the majority of the world population. For this, production of efficacious food products and pest control agent in collaboration increases the effectiveness of crop diversity. By virtue of Nitrogen Using Element (NUE) in plants, a traditional nanofertilizer system doesn't compile the essential plant nutrients in practice. Several approaches were used to make a cost-effective nitrogen-fertilizer system as a source of nutrient for plant. Rather than nitrogen, urea acts as an effective source and will be site-specific which helps in proper nourishment of the plants. This study aims to develop inexpensive, expandable and a powerful nitrogen-fertilizer system which decelerates solubility of nitrogen by a least of five times contrast to pure form of urea. Even a bio-synthetic material, calcium carbonate ($CaCO_3$) provides benefits of nontoxic environment with physiological-compatibility. In-situ synthesis of Urea-$CaCO_3$ nanocomposite via fast carbonization method produces cubic-plate-shaped nanoparticles which were builds together to organize pine cone-shaped structures. The FTIR spectroscopic results were revealed the integration of urea with $CaCO_3$ which provides an effective platform for limited discharge of urea. X-ray diffraction technique was used to studied crystallographic information of Urea-$CaCO_3$ nanocomposite. Furthermore, it has been concluded that due to nitrogen releasing nature of urea-modified-$CaCO_3$-nanocomposite used as a novel, efficient nanocomposite which had the ability to substitute the traditional fertilizer system into prolonged food security (Rathnaweera et al. 2019).

3.4 Control of Plant Pests

Plant diseases caused by several phytopathogens can be successfully restricted by adequate concentration of nanoparticles. Fusarium wilt is a destructive disease of tomato and lettuce in several countries due to its severe production loss, prolonged survival of fungus in soil and generation of resistant races. Use of resistant chemicals and cultivators can help in its reduction to some extent. New pathogenic races are a chronic issue with expenses of chemicals adding to the problems:

Synthesized magnesium oxide with different concentrations were tested on green peach aphid (GPA) under greenhouse conditions. The blend of nanomaterials of [CuO + ZnO + MgO] was tested using *Punica granatum* peels, *Olea europaea*, *Chamaemelum nobile* flowers. Tests founded the fact that the above nanoparticles are efficient to increase the mortality of green peach aphid. Blend of metal oxide nanoparticles were tested in fruits and leaves of green sweet pepper. No metal accumulation was found in any of plant fruits. Mostly used nanoparticle is nano silver, as it has high prohibition rate and affects bactericides. It consists of wide range of activities for antimicrobes. High antimicrobial activities of nano silver as compared to bulk silver can be attributed to large surface area and more power of fraction to surface atoms (Ghidan and Antary 2020). Rose powdery mildew is occurred due to sphaerotheca pannosa var. rosal, is a far-flung standard illness of greenhouse and roses which are grown outside. Less flowering, leaf distortion, initial defoliation and curling of leaf are its main consequences. Reactions which are caused chemically by silver ion with reducing effect and stabilizers provide double capsulated nano-silver. Its stability is more and it is fully dispersed in liquid solution. This destroys useless microorganisms which are found in soil that is used in planting process and hydroponics system. Basically it acts as a foliar spray to inhibit fungi and moulds. Silver is magnificent plant growth stimulator. Nanotubes of aluminosilicates when sprayed on plant surfaces are easily traced in insect hairs. Insects readily take nanotubes which are filled with pesticides. These are highly active and highly ecological in nature. Silica nanoparticles which are mesoporous in nature are a powerful tool for transportation of DNA and chemicals into plant cells (Singh et al. 2015).

Titanium oxide (TiO2) used to manufacture paints, ink, cosmetics; leather is a non-poisonous pigment of white color. It is powerful disinfectant with more efficiency than chlorine and ozone. Its nontoxicity results in its utility in food stuffs up to 1% of final weight of item. Titanium oxide (TiO2) photo catalytic technique possesses high pathogen disinfection efficiency protects plants and avoid to forming poisonous and harmful compounds (Satti et al. 2021). 20/40/60/80 mg/L of TiO2 NPs were sprayed on wheat plants which were consumed by fungus *Bipolaris sorokiniana* (cause blotch disease). This disease incidence and % disease index were measured and 40 mg/L was found to be the most accurate amount of titanium oxide nanoparticles that leads to decreased harmful effects of illness. Biologically formed titanium oxide was tested for morphology of agriculture like (fresh dry weight of plant, leaf, surface area, production measures and root), metabolites having non-enzymatic action like (soluble phenol, soluble sugar, flavonoid content and proteins), effects on physiology like (chlorophyll content, relative water content and index of membrane stability) during biotic stress in wheat plants. Titanium oxide nanoparticles can surely increase the quality and yield of wheat (Satti et al. 2021). For better luminescence, small emission spectra, excellent photo stability and tenability, Quantum dots are way ahead than organic fluorescent dyes. These broad absorption spectra allow quantum dots excitation to all colors. To detect pathogens quantum dots come to our help. Witches Broom Disease of Lime (WBDL) occurs due to phytoplasma aurantifolia founded by sensors which are based on energy transfer by QD resonance. Sensor with specificity of 100% and detection limit of 5 aurantifolia per μL was developed. Beet necrotic yellow vein virus causes Rhizomania in sugar beet. QDs sensor detected the Polymyxa betae [Keskin] which is a vector of Belt Narcotic yellow vein virus (Khiyami et al. 2014).

3.5 Nanoherbicides and Nanopesticides

In almost all developing countries, agriculture always is a backbone as more than 60% of total population completely depends on it for their living. Nanotechnology is somehow enhancing terms of biology for various crops and so actively increasing growth or nutritional values. Side by side nanotechnology help in development of various high technology systems for regulating environment conditions nutrition level or giving pesticides in exact amount. With that, nanotechnology gives areas to add value of crops or surrounding remediation. A good example of particle farming that gives nanoparticles for utility of industry via sowing different plant in definite soil. With the help of research we get to know that alfalfa plants which grow in soil that is rich in gold absorb gold nanoparticles with their roots and invest them in their tissues. From plant tissue the gold nanoparticles can easily discrete by mechanical method that is followed harvest (Ameta et al. 2020). As biopesticides come into view, they can decrease dangerous outcomes of synthetic pesticides. But there is limit in utilization of biopesticides because of their steady and surrounding dependent potential against best. Feasible efficiency of nanoparticles is to overcome these hindrances. For a long period of time nanomaterials played a significant role in pest control due to their steady degradation and have a check on discharge of active ingredient. So due to this, nanoparticles play vital role for sustainable and efficient to reduce the utility of synthetic chemical and the threats related to surrounding (Chhipa 2017). According to researchers nanoformulation in permethrin consumption is more than the commercial form besides Aedes aegypti. Nanopesticides decrease the harmful impact on plants and soil bacteria (Suresh Kumar et al. 2012). By putting nanoformulation of carbofuran and acephate based on polyethylene glycol gave the similar results. Some findings are found when commercial product of acephate gets compared with nano acephate to nano-target organisms, which they have less toxicity (Usman et al. 2020). Some suggestions acknowledged that effectiveness was not enhanced due to more uptakes of nanoformulated active ingredients but it is increased to slower liberation of active ingredients. Chlorfenapyr which are attached with micro-particles get combined with silica nanoparticles (Iavicoli et al. 2017). New studies signify that nanosilica has great efficiency to regulate insect pest of grain products that are found in ion storage condition (Gamal 2018).

Hashem et al. (Hashem et al. 2018) explained that higher effectiveness and strength of anise (*Pimpinella anisum*) essential oil in opposition to red flour beetle (*Tribolium castaneum*) and this gave a result that nanoemulsion could decrease the utility of severe synthetic insecticides in opposition to insect pests. Nanoformulated commercial fungicide (Trifloxystrobin 25% + Tebuconazole 50%) growth checked at numerous concentrations (5, 10, 15, and 25 ppm) in opposition to fungal pathogens (*Macrophomina phaseolina*) borne in soil gave higher quality of working in spite of commercial compound (Kumar et al. 2016). Like, avermectin is a type of pesticide that can inhibit neurotransmission in insects by the process of blocking chloride channel that have less life span because it can easily deactivated by UV on the area of activity of only 6 hours. Silica nanoparticles which have pores in their structure has 15 nm thick shed and pore with diameter of 45 nm has a capacity to encapsulated 625 g kg 1 for avermectin and give protection from UV rays for degradation. About 30 days earlier it was stated that encapsulated avermectin give slow liberation by NPs transporters (Ghormade et al. 2011). Energy and water can be conserved by nanopesticides as they are used in less quantity and also occasionally than conventional pesticides. They also increase productivity of crop and increase effectiveness of pesticide by more growth and less input costs via decreasing labor and waste price (Lade 2019).

Nowadays weeds are appearing as a new warning in field of agriculture. Nanoherbicides can upgrade potential of herbicides that depends fully on polymeric body which is biodegradable. Like poly (epsilon caprolactone) is utilized to record atrazine payable with high quality of increased biocompatibility and bioavailability and its physicochemical possessions (Abigail and Chidambaram 2017). Polymeric nanoparticles recorded along with atrazine, had shown efficient role on targeted plant along increased action of herbicide, decreased fluidity in soil and stabilized activity of herbicide (for 3 month) as contrast to atrazine free form (Pereira et al. 2014). Same type of work was showed in other works with recording based polymer of various herbicides (simazine, atrazine, paraquat, and ametryn) (Usman et al. 2020). A plus in herbicide bioavailability show somehow same or little enhance effect of glycophosphate nanoemulsion as compared to commercial formulation (Usman et al. 2020). Areas which are prone to rainfall herbicides application along less soil moisture cause loss in form of vapors. As application of herbicides is not possible in progressed awaiting rainfall as predication of rainfall can be possible significantly. Regulated liberation of recorded herbicides is supposed to give an eye on progressive weeds with crops (Roy et al. 2014). In opposition to slender amaranth (*Amaranthus viridis* L.) and hairy beggar ticks (*Bidens pilosa* L.) nanocapsules containing atrazine give most efficient work as compared to commercial atrazine items (Sousa et al. 2018). So nanoformulations are emerging as the most efficient nanoherbicides to regulate weeds in a proper way.

By a significant association of anionic lingo-sulfonate with epoxy coating containing nanocarriers, integrated with abamectin were produced a modern lignin-modified-electronegative pesticide nanocarrier. The outcomes showed that negatively charged nanoparticles have an adequate size of 150 nm with 93.4% efficacy of abamectin for encapsulation of nanocarriers. However, polymer based nanocarriers may inhibit early release of abamectin and preserve active components from microbial deterioration. The intensity of soil adsorption to abamectin was loaded in nanocarriers for impressive flexibility of soil. In the meantime, nanoparticles might be able to pass through the roots and nematodes. The software testing established that controlled impact of this novel pesticide was 26–40% greater than that of other chemicals used in agriculture. Regardless of its excellent biological activity and employment ratio, transportation system of this novel pesticide has advanced potency to regulate plant-parasitic nematodes and also refines the efficacy of pesticides usage (Zhang et al. 2020a).

Toxic chemicals and other compounds which are harmful to living can be easily found out with the help of nanotechnology. Many useful functions are performed by nanoparticles which are combined with antibody can give light to find out some substances, it is also used in agrochemical for quantification and labeling like pesticide. Decontamination of water is caused due to residues of pesticide; coupled nanomaterials with any material can be used in photo catalysis; the process by which reactive of light along with some material can remove them (Alvarado et al. 2017). Working of photo catalysis is studied by combining it to nanotechnology, nanotechnology itself give good outcomes and also give a new way to delete compounds like analgesics (acetaminophen and antipyrine), bisphenol, o-phenylphenol, testosterone, caffeine and herbicides, fungicides and bactericide are used for analytic effects. Oxidation process which depends on photo-Fenton oxidation and solar radiation is used to remove mentioned compounds for catalyses with iron or ozonation and TiO_2 (Hernán 2015). Metal nanoparticles or oxides of metals can only be used for photo catalysis example: Au, TiO_2 (widely used), Fe_2O_3, ZnO. For photocatalytic property, nanoparticles give physiochemical and optoelectronic effects (Alvarado et al. 2017).

3.6 Soil Fertility Management

To maintain crop quality, fertility of soil and high yield of food, fertilizers are used. Basically fertilizers are come in more use after more production, hybridization and cultivators which gave quick response to fertilizers. Methods that are used for fertilizers (like spraying) lead to loss due to water runoff, hydrolysis, which causes drainage of soil moisture, leaching, evaporation, drifting, and degradation of phytolytes and microbes. Due to this loss, very low amount of fertilizers moves to their target point. More amounts of pesticides and fertilizers are need for usage due to its loss in environment in form of 50–90% potassium, 40–70% nitrogen and 80–90% phosphorous (Pramanik et al. 2020). Many side effects in environment are seen due to high and enormous amount of fertilizers and pesticides which are as following; contamination, pest become resistance to pesticide reduces soil fertility, degradation of natural resources and also leads to decrease micro flora of soil, decrease nitrogen fixation and enhance bioaccumulation of pesticide. So use of intermediate amount of chemical and synthetic fertilizers is accordance with their nutritional demand of crop, and it leads to decrease pollutants in environment. Nanofertilizers are act as fertilizer with smart feature that can give one or more nutrients to plant growth and production of crop (Liu and Lal 2015). At nano-meter level, nanofertilizers behave as a product of it which provide nutrition to targeted cell and also increase the efficiency/effect of nutrients and reduce degradation of environmental (Pramanik et al. 2020). To increase the capacity of soil to hold water, nanozeolites, hydrogels and nanoclays are used, as they are the source which liberate water slowly, decrease the time of hydric shortage at the time of cropping. These systems are beneficial in terms of the areas which are utilized for reforestation and for agriculture usage. To decrease time and amount of treatment, to absorb pollutants release from surrounding and to enhance remediation of soil, various inorganic like nanoparticles of metal oxide and metals, organic compounds like nanotubes of carbon and polymers are used (Duhan et al. 2017).

3.7 Nanomaterials as Priming Agent (Nanopriming)

Nanopriming is a technique where nanotechnology is used to increase seedling vigor, seed germination and growth performance in all plants (Mahakham et al. 2016). Mahakham et al. galangal rhizome abstract is used to prepare gold nanoparticles; these abstract are worked as a medium of nanoprimer to countersign the yield and germination of maize seedling. He detected the usage of gold nanoparticles which are formed by using abstract of Kaffir lime leaf to enhance the germination process of aged seeds of rice. Nanocomposite which are photosynthesized was utilized as activator that (a) increase uptake of water, (b) give species which are more oxygen reactive, (c) enhanced the activity of alpha amylase, (d) activate hydrolysis of starch to attain growth of embryo, (e) give growth to seedlings (Mahakham et al. 2017). Different techniques used for characterization outcomes shows a great AgNPs formation that are capsulated via photochemical which are basically plant extract. Rice aged seeds are encapsulated with silver nanoparticles which are phytosynthesized at 5 and 10 ppm which markedly enhance the process of germination and vigorous seedling in comparison to unprimed control, $AgNO_3$ priming and traditional hydropriming. α-amylase working can be increased by nanopriming that gives rise to more content which is sugar soluble to give a support to growth of seeds. In seed germination process, genes which are aquaporin in nature are activated by nanopriming. Along with that time, it was observed that nanopriming treatment of germination of seed give high product of ROS in comparison to different priming tools and unprimed regulation. This point gives the information that aquaporins and ROS both give major role to increase germination of seed. Many methods including induction of seed germination by nanopriming were suggested, which consist of nanocatalysts which are used to speed up hydrolysis of starch, nanopores used to increase uptake of water, hydroxyl radicals formation to loosen cell wall, restarting ROS system in seeds (Mahakham et al. 2017). Guha et al. founded zerovalent (nZVI) iron nanoscale act as a nanoprimate that helps in advancement and growth of *Oryza sativa*. In aromatic cultivator of rice named as *Oryza sativa* cv. Less amount of nZVI-based nanoparticles was found to increase their growth potential which acts as an agent of seed priming. By using various amounts (Nair et al. 2010; Rai et al. 2012; Usman et al. 2020; Khiyami et al. 2014; Mausavi and Rezaei 2011) of nZVI nanoparticles, priming of seed occur and permitted to grow about 14 days. Along with various points of times, by checking structural, physiological and biochemical parameters, production of seedling and seed germination were evaluated. Highest working of enzymes which are antioxidant and hydrolytic, and the enzyme help in dehydrogenation of root were found in 200 mg/L^{-1} nZVI primed seeds. Vigoursity of seeds is enhanced by priming seeds with less amount of nZVI, vigoursity is shown by more length of stem, high biomass, more root length and more amount of photosynthetic pigment (Guha et al. 2018). Sayedena et al. found the effect of nanopriming, utilization of multiwall carbon nanotubes (MWCNT) on development of mountain ash. This work showed that treatment of nanopriming enhanced the moisture content of seed and infiltration of seed dormancy and causes seed germination. Species that are endemic somehow do not consist of mountain ash (*Sorbus luristanica* [Bornm]) dormancy. In mountain ash best germination of seed and seed dormancy breakage can be done with the help of more effective multiwall nanotubes of carbon. Priming of seeds is done by various amounts of nano-materials which consist of (250, 75, 150, 500, and 350 mg L^{-1}) for nearby 24 h. After this above step two types of stratification process occurred, that is, warm (for two weeks) and cold (for 3–4 months). Above observations concluded that stratification under cold condition need three months at least for seeds. Then after the process of stratification in cold, Petri dishes are used to transfer seeds in germinator. For 22 days, germination of seeds was observed on regular basis. During this time period various measures were seen and evaluated during germination of seed like mean time for germination, % age of seed germination and speed of germination process (Sayedena et al. 2018).

Very less findings told about the impact of carbon dots on production of seed and germination of seed. Work performed on Zea may analyze that more amount of CDs (i.e., 1000 and 2000 mg/L^{-1}) provide low stem and root biomass because of the deposition of H_2O_2 and lipid in intensified form per oxidation. Some enzymes we get active due to CDs which are antioxidant in nature (e.g., SOX, APX, CAT, GPX) are found in cells of root cap, mesophyll cells of leaf, in root's vascular tissues and cells of cortex, showing the great efficiency of translocation and absorption in maize plant of CDs. With the finding, some results were found regarding the removal of CDs from leaf blade (Chen et al. 2016). Mung bean (*Vigna radiata*) sprouts were given more CDs with a range of (0.02-0.12 mg/L^{-1}), and this had an impact on concentration-dependent results because the sprouts produced more carbohydrate, a high biomass production, and larger roots and stems due to less CDs. With respect to that CDs increased the amount of chlorophyll and also increase the working of RuBisco to give effective photosynthesis in sprouts (Wang et al. 2018). Raja et al. funded that in vitro conditions for seed priming of blackgram (*Vigna mungo*) ZnO and Cu nanoparticles are added to it. The working which was done in vitro circumstances where treatment of seeds is done by various amount of nanoparticles of Cu and ZnO, in which zinc oxide nanoparticles and nanoparticles of copper were kept in liquid solution in amount 600 mg/L, 400 mg/L for about 3 h and they get dried with nanoparticles of ZnO and Cu for about 1100 mg/kg and 900 mg/kg to enhance quality of seed in blackgram (Raja et al. 2019).

Risk of climate change, depletion of resources and biodiversity is threatening our agriculture. Nanotechnology can be a feasible solution to this threatening situation. The effective process of seed nano-priming can alter the metabolic and signalling pathways of seeds, which has an impact on all stages of plant life, including germination and seedling establishment. Studies have demonstrated a number of advantages of seed nano-priming, including enhanced plant growth and development, increased productivity, and better food quality in terms of nutrients. The use of less pesticides and fertilisers is made possible by the modulation of biochemical pathways, the equilibrium between reactive oxygen species and plant growth hormones, and the promotion of stress and disease resistance. Toward sustainable agricultural practices, the present review gives the pros and consequences of the use of nanotechnology in nano-priming (de Espirito Santo Pereira et al. 2021).

Agriculture which is dome for market level should have regular and high speed of seed germination for great establishment in field of market (Mahakham et al. 2017). The process of taking water by mature seed is the initial step of germination, process of germination get stop with axis elongation of embryo, via seed coverage that leads in swelling of stem and root. Plant yield, its growth and development all are the basic characters of plants which get base from the process of seed germination. Natural process of germination includes more time and high crop production is also less. Seeds which are treated have high speed of germination. This process leads nanotechnology to act as a useful method that increases germination and production also. To boost the process of germination many researchers were found to regulate the efficiency of nanoparticles. According to a research, by using nanoparticles of silver, carbon and gold we can regulate the process of germination step by step of *Trichilia dregeana* (Recalcitrant) and *Vigna radiata* (Orthodox seed). By above studies we get to know that nanoparticles of silver and gold are the inhibitors of speed of germination while nanoparticles of carbon leads to more growth in stem and root in both the above plants remarkably (Mohanlall et al. 2013). According to research single walled nanohorns carbon enhance the process of seed germination in six plant species that are; maize, tobacco, switch grass, rice, tomato, soyabean, barley (Milewska-Hendel et al. 2016). Late and slow seed germination can be seen in spinach by giving it a treatment of CeO2 and nano iron pyrite (FeS2) (Das et al. 2016). This information can be utilized to slow and late seed germination, also used to change population of weed, give high energy effective plants, storage of seed during harsh conditions maintain life cycle timing of plants mainly in the region which get limited sun's energy. Seed primers have nano-CuO help to detect remarkable decease in seed germination in rice plant. At the point of 2000 ppm Cu show inactivation of seed germination in soyabean and chickpea having copper oxide nanoparticles. Effect of copper sulfate solution on soyabean and chickpea seed germination is used to see the results of following experiment at any concentration, that is, low as 200 pm because of more stress by salinity (Shukla et al. 2019).

Less amount of graphene leads to give a great impact on growth of seed and germination of seed in tomato plant. The seeds which are treated by graphene germinate speedily as compared to control seeds. By analysis, scientists found that seed husks are stimulated by graphene. Stimulus by graphene results in breakdown of seed husk that increases the uptake of water which leads to increase rate of germination and speed up process of germination. During the time of growth of seed, graphene leads to stimulate cells of root tip. By analysis, scientist find that other than different nanoparticles, graphene give a significant role in growth of seed, as graphene treated seeds during the time of germination of seeds give lengthy root and stem and have less accumulation of biomass in its body as compared to control seeds. By joining the entire above conclusion we found that initial phase for growth of stem and germination of seeds is highly effected by graphene. Amount of graphene caused high impact on initial growth of plant. High amount of graphene somehow leads to genotoxicity and oxidative stress, while as it can help in transportation of water it enhances germination process of seed. (Zhang et al. 2015).

3.8 Nanobionics and Photosynthesis

More than an enhancement in amount of factors related to agriculture, it is a fact that indicates that quality effect of photosynthetic process leads to good quality in crop production. More recently a key idea to add nanomaterials with living plants to enhance their native function and providing them non-native function has more precisely targeted. This theory give the main of “plant nanobionics” (Giraldo et al. 2014) and actively permit to give rapid plant growth and become the main aspect to enhance and develop system of artificial photosynthesis that is the main way to swipe away energy (Noji et al. 2011; Singha and Bell 2016). With this it also cause many more ideas which can’t think at this period of time. Research categories from Massachusetts Institute of Technology (MIT) gave first post giving an action on nanobionics of plants. Single-walled carbon nanotubes (SWCNTs) in suspension were perfused into isolated Spinacia oleracea chloroplasts and Arabidopsis thaliana leaves. Electron transport rate is enhanced by 2 h with the help of this procedure in comparison to regulate isolated chloroplast shelf life. Having an eye on these researches, researchers find out that SWCNT-chloroplast congregated advanced nearby three times action of high photosynthesis than increased and regulate rate of electron transport (Giraldo et al. 2014). Photosynthesis process show positive outcome of nanomaterial, as recorded by many research papers. Anatase crystal $nTiO_2$ having catalytic action due to which it play it play vital role in the productivity of light absorbance via leaves of plants that remark an enhancement in the process of photosynthesis. It was recorded that TiO_2 prevent aging of chloroplast because of stress caused photochemical and by this (Zhang et al. 2020b). Rubisco carboxylation activity cause high rate of photosynthesis (Siddiqui et al. 2015; Mohammadi et al. 2016) and biophysics characters of photosynthesis, action of chl-photophosphorylation and electron transport chain also get effected (Qi et al. 2013). Along with photosynthesis $nTiO_2$ also helped in water conduction and increased rate of transpiration of leaf (Chaudhary and Singh 2020).

3.9 Nanotechnology in Food Packaging

Food needs to be stored for longer run. Food packaging is the vital part for food supply chain. Proper food packaging protects food from contamination, dirt and preserves its food quality. Safe, inert, lightweight, easy disposition/reuse, stress proof comes under the net of an ideal food packaging material. To decrease environmental stress and increase shelf life, impermeable packaging nanomaterials is used so that food is protected from UV radiation (Shukla et al. 2019). To detect chemicals, pathogens and gases, nanosensors came our way. All this come under one net term of Smart Packaging (Ghidan and Antary 2020). To increase the surface area of fibers, size of nanofillers is reduced. High surface area leads to large boundary area between matrix and nanofillers. This modifies the molecular mobility, relaxation behavior along with mechanical and thermal properties of bio-nanocomposites. Bio-nanocomposites are capable to persist the mechanical and thermal stress caused in food supply chain. The performance and biopolymer is increased by many types of nanosized fillers (less than 100 nm). To study the properties of Bio-Nanocomposite, researchers gave some experiment with different type of fillers and biopolymer. Study of physiochemical properties of antimicrobial composite film [nanoparticles of gelatin, silver; hermos chemical and morphological properties of bionanocomposite film (Wheat gluten matrix, cellulose), physical properties of bionanocomposite film (fish gelatin, ZnO nanorods) is done extensively. Fillers that are nonosized could be oxide of metal (like titanium oxide), inorganic, organic (clay, montmorillonite MMT), metal (copper), natural antimicrobial agents like (Nisin), natural biopolymers (e.g., Chitosan) (Othman 2014).

3.10 Nanotechnology in Agriculture Machinery

In the agricultural machinery area, nanotechnology has various relevancy that is it works in structure of machine and agriculture equipment to enhance their opposition power toward corrosion, tear, and UV rays give powerful mechanical composition by using nano-coating and biosensors in high-tech machines for chemical and mechanical control of weed, give nanocover to bear decrease in friction. To decrease environmental contamination difference fuels are produced by the utilization of nanotechnology (Mausavi and Rezaei 2011). The hard-working conditions for agricultural machinery and equipment, especially tractors, combines and other machines used in fields or gardens, further specify the need for utilizing more durable parts. Using nanoparticles of clayey soil and carbon nanotubes to produce nanocomposites with improved mechanical properties compared to conventional composites can be a new approach to lightening and even replacing metal parts in agricultural machinery. Nanocomposites are a new category of materials that include old polymers reinforced with nanometric particles, and in fact nanocomposites are a group of plastics full of minerals that contain a small amount (less than 10%) of nanometric particles (often clay). Theoretically, these materials can be easily extruded or molded in the final shape, while they have the same strength of the metal and are lighter. This not only affects increasing the life of this equipment, but also lightening them, reducing fuel consumption and, consequently, reducing environmental pollution (Dehkordi and Keivani 2017). Tire is one of the most expensive parts of a tractor or combine that can be used to increase the tire's tilt resistance and reduce the wear of tire up to 50% by adding nanoparticles to the tires of tractors and agricultural machinery. The presence of nanoparticles in the structure of tire increases wear resistance, strength (improving the mechanical properties of the fracture) and the apparent beauty of the tire. Moreover, it also brings the smoothness and elegance of the appearance of tire. All of these factors produce a high quality product that can last longer in a variety of conditions for tractors and combines. By adding these nanoparticles to the tire, the amount of butyl rubber required for the tire is reduced, and the tire becomes lighter and cheaper and remains cooler while moving. Today, nanotechnology has created a profound transformation in the industry (Razzaqi 2010). The properties of these types of tires include:

- Increased the resistance of tires to wear
- Increased mechanical strength of tires
- increased the thermal resistance of tires
- Reducing the flammability of tires
- Improving tire heat distortion (Razzaqi 2010).

Nanocrystalline materials produced by Aero-Gel method can be used as materials for intelligent glass. This glass becomes dark and opaque when exposed to intense sunlight, and when sunlight shines less, it becomes brighter. This feature causes sunlight not to annoy the tractor driver’s eyes. In addition, since agricultural machinery is used in dust-free environment, this type of glass has its own self-cleaning properties, which is an important feature of the glass used in the manufacture of agricultural machinery and equipment. Nano-lubricants have billions of spherical nanoparticles that significantly improve friction and wear, as well as the compressive properties of the lubricant. The advantages of using these materials, depending on their function, can be to increase the speed and reduce the energy required, increase the life of the materials and reduce their environmental damage. In order to reduce engine erosion, copper nanoparticles are added to the engine oil, and ferromagnetic nanoparticles are used both in the structure lubricant and in the stopping leak structure. Fullerenes are also used to increase lubrication and reduce viscosity of lubricants (Ndukwu et al. 2020). Most products require adequate coating to prepare for acceptable market entry. Nanotechnology can be used to increase resistance to various environmental factors, for instance resistance to corrosion, the creation of new ability at the surface, such as hardening. Presently, considering the growth of nanotechnology and its use in various fields, coating can be considered as one of the most important sectors in the use of this technology. Nanometric coating for various purposes like increased strength, improved bending and shear properties, protective coatings resistant to corrosion, scratches, wear, and environmental factors, uniform distribution and reduced the use of chemical solvents in coating of the parts, and increased chemical and thermal stability are among the achievements of the application of nanotechnology in the production and manufacture of parts related to agricultural machinery and equipment. Moreover, the use of this technology in agricultural machinery in addition to improving equipment resistance to wear, corrosion and dust increases their useful life (Razzaqi 2010).

3.11 Nanoparticles in Recycling Agricultural Waste

Waste materials generated directly by agricultural practises or by industries connected to agriculture are referred to as "agrowaste". Every year huge amount of agrowaste is released. Industries works in field of biotechnology used as a big part of agriculture waste as raw material. Waste water or polluted water which get discharged from field of agriculture and food industry. Different forms of nanoparticles can be formed by agrowaste. All around the world, loose of huge amount of agricultural products and food in form of agrowaste every year. After calculations of human's food consumption, about 1/3 food formed become a waste every single year (most of 1.6 G tons accordance with the estimation of one). Apart from that previous report, new estimation comes under this which says that whole sum 6 G tons food and non-food agricultural material is lost per annum. We can estimate that, as if we decrease loss of agriculture products till this extent, surely we can release a constant pressure on our resources. Due to this, demand of food accessibility getting enhanced day by day for high population rate that leads to decrease the utility of chemical pesticides and fertilizers (Javad et al. 2020). Issues regarding wastage of crop nearby 80% of biomass of agriculture become a very highlighted and sensitive issue during the time of crop harvesting. Burning of agrowaste by farmers causes the release of many gases to the surrounding in huge amount. Burning of these gases causes high amount of smog (fog + smoke) and that give a great danger to normal human being body. Agrowaste can easily reuse, recover, and recycle in a strategic process within an hour to manage the agrowaste (Krishnaswamy et al. 2014). Proper and managed use of agrowaste must be a remarkable step in statics of economy and progress. Agrowaste is used in so different ways such as in formation of items that are derived from biotechnology, nanoparticles formation, and in formation of manure and biofuel, etc. The remains of agricultural items like feed, food and fruit and agriculture consist of agriculture lignocelluloses (Chandra et al. 2012). For many items of biotechnology like high protein, aromatic compounds, organic acids, microbial pigments, nanofillers, secondary bioactive metabolic products and enzymes, these waste could act as a raw product (Tepe and Dursun 2014).

As maize is used to yield ethanol, its demand in worldwide market was increased from last two years. Nowadays stock of cellulosic feed play a vital role in yielding of biofuel and nanotechnology. It also increases the working of enzymes that major play role to change cellulose into ethanol. Researchers start doing work on enzymes that are nano-engineered which leads easily and low cost change of cellulose which we get from parts of plants which are now of no use to change in ethanol. By product of rice milling and rice husk act as a new origin to inexhaustible energy. A best quality of nanosilica in high doses is formed while burning of rice husk and get changed it into biofuel and thermal energy, it could be used for various purposes, that is, formation of different items like concrete and glass. Regular origin of rice husk leads to high formation of nanosilica with the help of nanotechnology that leads to boost up the disposal issue of production of rice husk (Fraceto et al. 2016). Mainly in the cotton industry, nanotechnology is used to avoid pollutants. During the time of formation of fabric or cloth from cotton, many extracts of cotton-like cellulose and fibers of cotton act as a pollutant or utilized in making low-priced items like cotton bolting, balls of cotton and yarns. With the help of electro spinning method and newly formed solvent, experts provides fibers which acts as a fertilizer with a diameter of 100 nm. Absorbents with high activity permits achieved application on right time and place (Ghidan and Antary 2020). Rice husk can act as a good source of renewable energy; it is produced as a byproduct of rice-milling. Best qualities of nanosilica that can be used in formation of different types of items like concrete glass is formed by burning of rice husk and convert it into biofuel. Concern regarding getting rid of increasing amount of rice husk can be resolved as burning of rice to more amount of nanosilica with the help of nanotechnology (Phenny 2018). A well-organized biological method referred as aerobic digestion is the most efficient method which is used to convert pollutants of agriculture into methane gas (Nasr 2019). To save other energy resources biogas is a best renewable agent of energy which is used to produce heat, electricity and also help in cooking. Activity of enzymes and pathways related to metabolism of methanogenic bacteria is stimulate by the process of anaerobic digestion for which many essential elements are required, that is, Cu, Ni, Co, Zn, and Fe (Ganzoury and Allam 2015). For a chance, Abdelsalam et al. (Abdelsalam et al. 2016) interrogate use of metals as nanoparticles to promote the process of manure of anaerobic digestion.

3.12 Commercial Applications of Nanotechnology in the Agricultural Sector

When we are watching from business way, the agrochemical companies which are already present in market getting the ability of nanotechnology and in some way if artificially formed nano-sized active material could enhance the effect or give a stimulus to the components which are beneficial in plants. Till now nano-sized particles are unable to hold main useful changes in product physiology, mainly if we are planning for a high scale production with high cost. In market, some small companies which are mainly technology based gave some nano-products which are useful in field of agriculture, like they launch a product which enhances soil productivity, distribution of water, save water and also help in storage. Ass per now, market-based companies that give nanoproducts are only ranging in small scale area, because of its high cost during production. Normally this high price can be figured out by having more returns in field of medical and medicinal areas, but we don't get any kind of benefit from agriculture area. To find out future benefits in the business-oriented agrochemical sector, research is regularly going on (Nanowerk Spotlight 2014).

4 Drawbacks of Nanotechnology

Despite of all above mentioned advantages there are some drawbacks of nanotechnology in agriculture field. Many issues have been increased about the efficient adverse effect of nanoparticles on the environment as well as on biological system-like generation of toxic free-radicals lead to lipid per oxidation and damage of DNA (Fig. 3). By employing these more potential techniques, lead to increase the number of nonemployment in the area of farming due to less requirement of human worker with these better operative techniques. Still researchers are in doubt due to lack of insight on processes that how far this nano-based technology plays a significant role in agriculture field, specifically they are concerned with the level of toxicity which becomes harmful whether products were consumed or while this will entering into living cells (Rienzie and Adassooriya 2018).

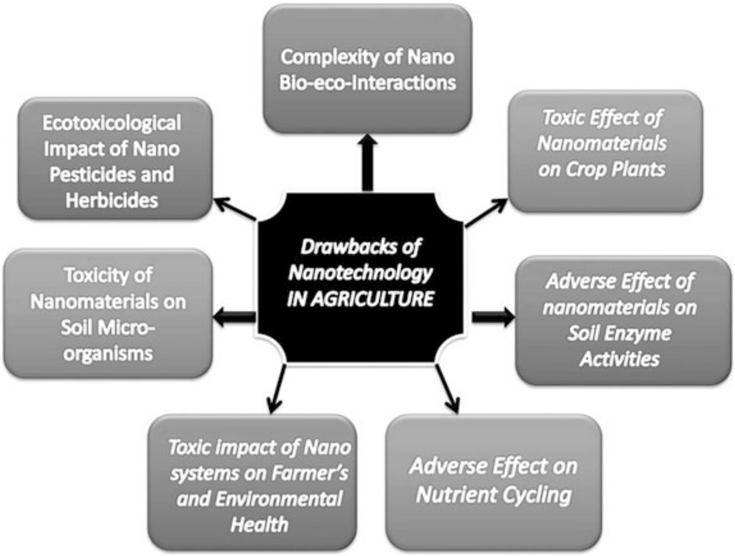

Fig. 3 Negative impact of nanotechnology in agricultural area

4.1 Demerits of Nanosensors

However, nanotechnology-based farming has created a novel and smart change to minimize accompanying risks. In agriculture field, due to improper guidance of using sensors and food products be a cause of worries on population health and ecosystem worldwide. Limited analysis of their behavior in soils is mainly due to their nano-sized complex interactions. For this reason, an integrated path has been recommended for interpretation of these fundamental interactions in ecosystem. Government authorized a legal framework of instructions followed with the use of nanomaterials to analyze toxic effects in the environment to a greater extent (Usman et al. 2020).

4.2 Demerits of Nanopesticides and Nanoherbicides

It is a well known of likely toxicity impact of nanopesticides. Earthworms are good indicators of soil health; their first ecotoxicological life was determined by Heckmann et al. Various types of inorganic nanoparticles were used to analyze the toxicity on earthworms. The complete reproductive failures of earthworms were observed with silver treatments (Heckmann et al. 2010). The reproduction of earthworms was remarkably minimized when they were treated with silver nanoparticles. However, it was reported that accumulation of Ag was higher in tissues treated with $AgNO_3$ as contrary to similar concentrations of Ag nanoparticles (Shoults-Wilson et al. 2011). Jośko et al. (2020) observed that high concentrations of oxidized Cu nanoparticles had harmful impact on earthworms. Atrazine used as an herbicide and to check the toxicity level in earthworms has been specifically reported on the basis of different lethal dose concentration at a specific time intervals. Comparably, tissue pathological studies showed breakage to the epithelial tissues and chloragogenous layer, prominent vacuolations and pyknotic cells (Nayak et al. 2018).

Compound belongs to triazine herbicides includes ametryn, atrazine, and simazine were commonly used for controlled effect of broad-weeds on crops like maize, sorghum, and sugar cane. Although their approval in agriculture field, herbicides can be harmful for environment depending on their toxic nature, level of contamination and exposure time period. A prolonged-delivery system has been progressively used to check dilemma of toxic behavior, reduce influence of environment and develop herbicidal productivity. In (Andrade et al. 2019), the author developed a polymer poly(ε-caprolactone) nanocapsule with a combination of herbicides via interfacial deposition method which were further used to analyze their toxicity to marine species. Eco-toxicity tests were done with the algal (*Pseudokirchneriella subcapitata*) and micro-crustacean (*Daphnia similis)* species. Moreover, cytological analysis of lymphocytic cells at varied concentrations represents alteration of mitotic index and also implied that encapsulated herbicides showed less eco-toxicity than the herbicides apart. Herbicides were capsulated into the form of nanocapsules which showed less toxicity toward algal species and more toxicity towards microcrustacean in contrary to herbicide apart. The results were suggested the efficiency of nanocapsule assembly tends to minimize the amount of herbicides used. Moreover, nanocapsules play a significant role in reducing the influence on human health and surrounding ecosystem. The findings were determined that poly (epsiloncaprolactone) encapsulated herbicides has showed lesser effect on *Pseudokirchneriella subcapitata* while *Prochilodus lineatus* has found much more toxic to the Daphnia similis contrary to non-capsulated herbicides (Andrade et al. 2019). Based on aforementioned risks and other toxicological studies of nanoparticles (Usman et al. 2020), suggested that general risk evaluation appeals for nanoparticles as nano-pesticides at biomolecular level. According to environmental protection agency (EPA, USA), nanopesticides may affects human health as follows: (a) skin epithelial cells absorb nano-pesticides with the help of their tiny size, they can easily pass through cell membranes, (b) via respiration by intercrossing a bridge between blood and brain, (c) environmental concerns raised due to reactive potential and durability of some nanomaterials and (d) lack of proficiency to measure environmental exposure with NMs (Lade 2019).

4.3 Adverse Effects of Nanomaterials on Soil Microbes

Presence of microbes into the soil indicates superior soil. Soil quality has direct influence on organic component of soil and nutrient cycle. So this, soil organic matter (SOM) directly influences all physio-biochemical characteristics affects high crop yield and decrease levels of global warming (Hegde et al. 2016). Various reports of carbon nanomaterials were investigated which resist changes in structure and composition of microbial community. In most of the microorganisms, carbon nanoparticles affect functional genes of archaebacteria and eubacteria which are involved in Carbon and Nitrogen-cycles. Authors studied the effect of carbon nanomaterials and fullerene (C_{60}) on structure and composition of soil microbial community. Microcosm experiments in combination of GeoChip microarray were performed to analyze the impact of fullerene and multi-walled carbon nanotubes (M50) which further transformed the functionality of soil microorganisms. The results were showing that M50 has major influence than (C_{60}) on working microbial genes. M50 had a vast and intense effect on microbe's nutrient cycles. Carbon nanomaterials largely influence biochemical pathways, suppressed nitrogen fixation process, proteins, lipids and metabolites. From various studies it has been established that carbon nanoparticles affects functional genes and soil microbial community which include only carbon and nitrogen cycle as sulphur and phosphorous was found less susceptible (Wu et al. 2020).

Previous studies determined that microbes present in soil were easily influenced owing to toxic nature of NMs (Remya et al. 2015). Especially, gram-negative bacteria were exposed to small-sized oxides of metal such alike titanium oxide and zinc oxide which instantly show decrease in microbial biomass carbon (MBC) level. Effects of nanoparticles on soil were caused reduction in overall biomass production and enzymatic activity, which directly influence microbial-biological diversity. Nanoparticles could pose a risk to human health (Simonin and Richaume 2015; Rajput et al. 2019).

4.4 Adverse Effect on Nutrient Cycling

N-cycle is naturally occurring aspect which can increases the production for long term use. N-cycle is correlated with productivity by influencing the microbes' accompanying with n-cycle will also influence the crop-efficiency. *Pseudomonas putida,* aerobically denitrifying bacteria were observed to be affected by carbon nanotubes because of variation in the temperature range and higher level of fatty acids (Rodrigues et al. 2013). Similarly, Bandyopadhyay et al. reported that *P. putida* were observed to be affected by ZnO NPs. The author (Bandyopadhyay et al. 2015) showed bactericidal effects toward *Sinorhizobium meliloti*, nitrogen-fixing bacteria by using ZnO NPs. TiO2 and ZnO NPs had adversely affected the order Rhizobiales by decreasing the bacterial community or lessening their diversity (Simonin et al. 2016). Because of negative influence on bacteria and fungi species ZnO nanoparticles were expressed as a nitrogen-mineralization material from organic matter in previous studies (Rashid et al. 2017).

Kumar et al. showed that Ag NPs had affected species of *Bradyrhizobium* accompanied with arctic soil to a greater extent. The possible harmful effects of 0.066% copper, nanoparticles of silica and silver in terms of high latitude (>78°N), we can give a check on soil by utilizing community level physiological profiles (CLPP), analysis of DNA and fatty acid methyl ester (FAME) assay, that consist of a technique called as denaturing gradient gel electrophoresis (DGGE) and sequencing. The conclusion of various findings were merged so that we can form a group in toxic indicator, that showed that among all these nanoparticles, nanoparticles of silver are the most poisonous to Arctic consortia. Regular researchers that depend on culture verified that the bacteria which are incorporated with community—identified plant, that is, *Bradyrhizobium canariense* which show high sensitivity toward the nanoparticles of silver. So we can say that arctic soil get polluted by silver nanoparticles is a major issue, and to solve and rectify this pollution is a prime concern for findings (McGee et al. 2017). The major effect of using SWCNTs is to minimizing biomass production of soil fungi which acts as primary decomposers which are significant in recycling of nutrients (Rodrigues et al. 2013; Jin et al. 2013). Moreover, soil fungi were reported to be adversely affected when treated with ZnO NPs (Rashid et al. 2017). It has been observed that soil microbial biomass carbon (SMBC) showed a remarkable decrease when exposed to various nanoparticles such as Ag/Ni/Co/CuO NPs (Antisari et al. 2015; Xu et al. 2015) and SWCNT (Jin et al. 2013).Copper oxide nanoparticles leads to decrease three main microbial working, that is, (soil respiration, denitrification and nitrification) at 100 mg/kg dry soil, while reduced measures (0.1 and 1 mg/Kg) have only few impacts. For many verities of soil denitrification was always be a prone microbial activity for nanoparticles of copper oxide but nitrification and soil respiration always affected in coarse soil that have less amount of organic matter. In addition to that, high reduction of microbial working in heterotrophs had been seen in wheat planted soil at 1 mg/kg for respiration of soil that is stimulated via substrate, this situation showed that presence of plant is not supposed to alleviate harmful effects of copper oxide nanoparticles to all living microorganisms. Above two tests explained that nanoparticles of copper oxide gave harmful impact on working of microbes in soil along with different physiochemical effects and earlier suspected to different agricultural means. Studies that are done in short period of time (hours and days) do not showed harmful impact of copper oxide nanoparticles that enhanced day by day (Simonin et al. 2018).

For the sustainability of ecosystem, nitrogen that is a main nutrient of ecosystem should regularly reformed via recycling process, lack of it leads to compromised functioning of ecosystem. Few stages that occur during the microbial changes of nitrogen compounds were functioning via few microorganisms which lead to be a functional species of ecosystem. Silver nanoparticles are widely used in industrial area which possibly causes harmful effect on species which follow microbial nitrogen cycle. Silver nanoparticles have great antimicrobial activity suspected to get a range via various means of exposure in natural environment. Via many ways to expose in natural environment, silver nanoparticles consist of high properties of antimicrobes. Silver nanoparticles in toxic behavior somehow cause great impact on few microbes which are functional in nitrogen cycle. In vitro conditions, silver NPs have harmful impact on denitrifying, nitrogen fixing and nitrifying bacteria (McGee 2020). $nTiO_2$ exposure leads to inhibit working of nitrogen fixation (EC_{50}-96 h of 0.4 mg TiO_2/L) and growth rate (EC_{50}-0.62 mg TiO_2/L) too. To show the amount and growth inhibition which depends on time, here Hom's law act as a model for inactivation. Amount of TiO_2 in toxic level is less influenced as compared to exposed time; this is determined by kinetic measures. The outcomes show that cyanophycin grana proteins give vital function in mechanism related to stress on exposure of TiO_2. This finding shows that activity of nitrogen fixation can be damaged by exposure of $nTiO_2$ in aquatic surroundings. So it possibly causes effects on biogeochemical cycles that basically include nitrogen and carbon cycle (Kumar et al. 2015).

4.5 Adverse Effect of Nanomaterials on Soil Enzyme Activities

Soil enzyme activities are used to predict level of proper soil functioning and damage occurs due to contamination. Chai et al. reported loss of function in activities of soil enzyme due to ZnO Nanoparticles. Ecotoxicity of ZnO, SiO_2, TiO_2 and CeO_2 nanoparticles on agricultural soil were checked at 1 mg per gram. The ecotoxicity was further analyzed on the basis of thermal metabolism, abundant working of enzymes and bacteria which is functional in nature. However, zinc oxide nanoparticles and nanoparticles of CeO_2 directly decreases the number of soil bacteria especially Azotobacter, blocks thermo genesis process and enzymatic activities. Whereas, TiO_2 nanoparticles had a larger impact on enzymatic efficiency and reduce the amount of bacteria present in soil. In addition, SiO_2 nanoparticles moderately raised the activity of microbial soil. Pearson's coefficient correlation analysis signified that parameters of thermodynamics had a strong interrelationship with abundant functional bacteria and enzymatic activity. Many studies had concluded that functional bacteria, process of thermogenesis, and enzymatic efficiency are viable for analyzing the toxicity of nanoparticles on agricultural soil (Chai et al. 2015). ZnO and TiO_2 nanoparticles extensively decreased enzymatic activity for various soils like: catalase, protease and peroxidase. The impact of TiO_2 and ZnO nanoparticles has been examined on growth of wheat and soil enzymatic efficiency under favorable circumstances. Together these nanoparticles decreased the biomass production of wheat. Moreover, TiO2 nanoparticles were kept in the soil for long-terms and pre-dominantly attached to wheat cell wall. Whereas, the ZnO nanoparticles were mixed up with the soil particles enables increase uptake of zinc by wheat plant. These nanoparticles elicit significant changes in enzymatic activity of soil. Proteolytic and catalytic activity of soil has been suppressed in the presence of the nanoparticles alike urease activity was remain unaffected. Therefore, it has been suggested that nanoparticles and there dissolved form were toxic for the soil environment (Zhang et al. 2019). Effects of MWCNTs were observed with a great impact on enzymes present in soils like soil phosphatase, 1,4-ß-N-acetylglucosaminidase, 1,4-ß-glucosidase, cellobiohydrolase and xylosidase. Two corresponding soil type studies were carried out on the basis of impact of MWCNTs on action and biomass production of microbes for a short period. A concentration of 5000 μg MWCNT per gram soil was used to analyze the activities and biomass of 1, 4-β-glucosidase, cello-biohydrolase, xylosidase, 1,4-β-N-acetylglucosaminidase, and phosphatase enzymes. Eventually, this study showed that both soil types were susceptible to be inhibited at 500 μg of MWCNT per gram and also all enzyme-mediated activities along with biomass production were substantially reduced up to 5000 μg MWCNT per gram soil. Hence, this clearly indicates that higher the concentrations of MWCNTs, lesser are the working of microbes along with biomass (Chung et al. 2011).

4.6 Toxic Effect of Nanomaterials on Crop Plants

Wheat crop were found to be beneficial to analyze toxic effects by using nanomaterials specifically metal based nanoparticles (e.g., Cu, CuO, TiO_2, Zn, ZnO, Ag and Fe_2O_3). CuO NPs showing their effect by limiting the overall growth, but eventually these NPs influenced the biomass production. Furthermore, they had adverse effects on several steps of photosynthesis of treated plants, by decreasing the chlorophyll content and elevate the peroxidase and catalase activities in roots (Amooaghaie et al. 2017). TiO_2 NPs has been found with greater impact on wheat plants as these NPs directly reducing the overall growth and yield (Zhang et al. 2019; Rafique et al. 2018). Out of these aforementioned metal-based nanoparticles, Fe_2O_3 were reported for its impact on germination of seed, which showed that at high concentrations it minimized the ability for seed germination (Rizwan et al. 2017). Hydroponically grown rice showed decreasing biomass ratio and disruption to the antioxidant system at the time of exposure with TiO_2 NPs. Additionally, TiO_2 NPs leads to change in specific metabolite concentrations inside the cells, reduction in carbohydrate synthesis process and increase respiration rate (Wu et al. 2017). Maximum concentration of CeO_2 NPs, elevated the H_2O_2 synthesis, while increasing the lipid-per oxidation and electrolyte discharge in rice plants (Rizwan et al. 2017).There are such many studies reported which demonstrated the toxic effect of many other nanomaterials (like Al_2O_3, MWCNTs, Si, SiO_2, and graphene) on different crop plants such as Maize (*Zea mays*), legumes, tobacco (*Nicotiana tabacum*), tomato (*Lycopersicon esculentum*), onion (*Allium cepa*), cucumber (*Cucumis sativus*), Pumpkin (*Cucurbita maxima*), *Brassica* spp., Red Spinach (*Amaranthus tricolor*), Cotton (*Gossypium* spp.), Radish (*Raphanus sativus*) and Lettuce (*Lactuca sativa*) (Rienzie and Adassooriya 2018).

4.7 Disadvantage of Nanotechnology in Food Packaging

High nutritive value food is making the food industries compete in a healthy way. Surveys and studies show that masses do not encourage the high impermeable packaging nanoparticles, material due to risky factors. To reduce the risk, industries needs to amplify the safety measurement net (Ghidan and Antary 2020). Nanomaterials have smart and unique properties so that they are integrated in packing-industries at a very high rate. Advantages of employing nanomaterials decrease whole packaging, build an active, smart and synergistic material having antimicrobial characteristics. They also delivered the material which increases the shelf-life of the packaged food and also plays a significant role in repairing of package when deteriorated. Smart nanotechnology has a great potential in food packaging, but it still has not been standardized. Many factors have been responsible for this included expensive manufacturing and distrust customer loyalty and also raise concerns due to environmental and administrative branch. Consumer product safety would become a leading concern with respect to utilizing nanomaterials. Various findings were suggested that the probability of translocation of nanomaterials from packaged food with the rate of translocation effectively coupled with the overall percentage of nanomaterials found in packaged material. Furthermore, severe major concern arises when a nanomaterial has been utilized as food nutritional content, it will constitute a severe-threatening condition to public health. Generation of ROS species induces cellular damage and death followed up by mechanism of toxicity. Excessive production of ROS species may cause auto-phagocytosis, destroy neuronal cells; diminished the DNA and ultimately leads to mutations, cancer, and aging problems in humans. Food supplements had adverse effects upon exposure with nanomaterials as they are having severe allergic reactions and damage metal. Moreover, the aggregation of nanomaterials in nutritive parts of plants and human anatomy can create obstacles at a maximum concentration and long-lasting interrelationships (Khan et al. 2011).

4.8 Adverse Effect of Nanotechniques on Farmers and Environmental Health

Different type of nanoparticles with wide applications in agriculture like organic, inorganic and carbon-based was discussed previously. For long-term use, nanomaterials may enhance ecotoxicological effects on an organism on exposure, intake which directly depends on its nanoness. In earlier, it has been discussed (Phenny 2018), most ENPs exist with exclusive properties only when they have an average size of 30 nm or less, which generally cause concern for human and environmental health. Toxicology tests have been carried out in vivo and in vitro to ensure safety level to the human health and environment system. To limit such difference in toxicological analysis, researchers are still trying to know the working of finest instrument that possibly will define the toxicity of the nanoparticles in agriculture field. Similarly, researchers were examined that nanoparticles enhanced its toxic environment via its charge-mass ratio, surface area and sample concentration. Knowledge of dose metrics responsible for toxic effects as stated by some researchers can have a number of advantages that includes ease of adaptation of the risk assessment data into the regulatory framework that ensure the safe use of such nanoparticles, particularly in agriculture (Iavicoli et al. 2017). Food and agriculture-nanotechnology has a great impact on growing population over the last decade. The action and fate of nanomaterials in nature environment is highly dependent and has physio-chemical characteristics which will raise a concern about human health and environment as some nanomaterials are introduced as food supplements and other inserted by virtue of emigration in various dietary and farming products. Further, interface of nanomaterials was used as nanopesticides, nanofertilizers, nanoherbicides and less often nanosensor which become cause of concern for environment. Moreover, the complex nature of environment restricts the predictive capacity of the action and fate of nanomaterials (He et al. 2019).

5 Future Outlook

In agriculture, nanotechnology plays a significant role in productivity, preservation and energy efficiency of the environment. However, the outlook has to be explored for long-term and pollutant-free application of nanomaterials:

- Favors public awareness and insight toward the beneficial impact of nanotechnology.
- Assure the association among nano-based science and technology, biochemical engineering, natural environment, and social advances.
- Develop a relationship among funding organizations and research organizations for a long period to endorse the effect of nanoparticles on human health and ecosystem.
- Elaborate research on function of nanoparticles which ought to be actively delivered water and nutrients to the plants for their proper development.
- Longitudinal study must be carried out to elucidate the association among nanofertilizers and structural soil and ecology. Moreover, in plants, it is necessary to manifest role of nanopesticides which were tissue specific and damage cell wall of soil microorganisms.

6 Conclusion

In this new era of nanotechnology, novel bio and nano techniques are found to be efficient in the field of agriculture. Nanotech-based applications play a significant role in manufacturing process and transportation of agricultural by-products. Nanotechnology will transform agronomy by innovating latest approaches which include accurate farming technology, increasing potential to metabolize nutrients, maximizing productivity, control of diseases with a specific detection, and endure environmental stress. To build smart nano-agriculture farming in future, nanoscale devices with smart processor will enhance efficacy of herbicides and pesticide for better yield. At present time the major emerging issue of using nanoparticles on ecosystem of agriculture has raised concern of adverse outcome and action of nanoparticles on crops and likely toxic association with plants and microorganisms that are present in soil surface area. Moreover, in nano-ecotoxicological state, DNA damage or lipid peroxidation process causes the adverse impact of nanoparticles on soil microbes, plant mass production and affects enzymatic activity of soil. Therefore before application of nanoparticles in agricultural field, their impacts should be observed and risk assessment studies should also be considered.

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Agronanobiotechnology: Present and Prospect

Abhaya Kumar Sahu, Swikruti Sonali Kar, and Punam Kumari

1 Introduction

Nanoscience, nanoengineering and nanotechnology offer plenty of a multitude of possibilities altogether. They demonstrate a practical recourse in the agriculture and agri-foodstuff areas, by offering a novel and progress scoring. In this light, we would like to share some recent advances in nanotechnologies and NM structures that could aid in food supply chain management and precision agriculture. Nanotechnology's applications and advantages in agriculture have gotten a lot of attention, especially in the development of novel nanopesticides and nanofertilisers.

Because of insufficient natural gas and oil reserves, production cost intrusions such as chemical fertilisers and pesticides are predicted to rise at an unprecedented rate. Several state-of-the-art methods for enhancing precision farming techniques are now available due to advances in nanotechnology, allowing accurate control at the nanometre scale. Nanotechnology has many applications in agricultural equipment, including increasing the resistance of machines and agricultural tools to wear, corrosion and ultraviolet rays through the use of nanocoating; the supply by nanocoating of durable mechanical elements and by biosensors for mechanical applications and chemical weed management in intelligent machines. Manufacturing of nano-covers for axes is to prevent friction. Nanotechnology is being used in the manufacture of alternative fuels to minimise carbon emissions. Nanotechnology has also demonstrated its ability to change the genetic constitution of crop plants to help improve crops significantly (DeRosa et al. 2010). Pesticides and chemical fertilisers were widely used during the green revolution, resulting in a loss of soil biodiversity,

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groundwater pollution and resistance to pathogens and pests. The provision of pesticides for safety purposes is becoming increasingly important in nanotechnology (Duhan et al. 2017). Nanotechnology in agriculture aims to minimise plant defence constituent dosages, reduce loss of nutrients, locate pathogens of plants, monitor residue of pesticide and raise output. A nanopesticide is a recipe used to maximise the effect of plant protection products using NMs as an active component (Saratale et al. 2018).

Agrarian nanotechnology is one of the main targets that needs immediate consideration in developing new nanocomposites capable of carrying active ingredients such as nutrients, fertilisers and pesticides. Farming programmes that focus on climate, recovering soil infertility and creating a new drought-resistant crop are among the other accomplishments that remain to be achieved to spread sustainable agriculture practices around the world. Furthermore, environmental sustainability and green chemistry principles must be built into nanotechnologies from the beginning. Consequently, investments in the growth and effective implementation of advanced agricultural technologies are crucial to enhancing agriculture and the food processing sector. In addition, to minimise food losses and increase food security, it can improve agricultural production, storage and transport (Shafiee-Jood and Cai 2016). Through systematic interdisciplinary research and efficient knowledge transfer, advanced analytical techniques are thus made possible using various kinds of NMs, interfaces and devices and their properties (Anderson et al. 2016). Electrical, optical sensors or electromagnetic sensors and electrochemicals are among the nanotechnology capabilities currently available in the market. Advanced wastewater treatment systems are proposed for effective wastewater treatment to overcome the lack of water supplies and low rainfall. The excessive use of mineral fertilisers and pesticides causes huge pollution and severe health problems (Yu et al. 2017). This improves the release mechanism and targeted mineral and nanopesticidal supply which shows better activity with an excellent protection efficiency compared to conventional pesticides.

Nanotechnology applications are unpredictable in farming due to its reliance on various natural components such as weather, season, water, soil, and agriculture. Therefore, the detection, registration, manipulation and storage of reliable and accurate data for both biotic and abiotic components are essential to addressing quality and food demand issues while ensuring environmental sustainability (Chhipa 2017; Servin et al. 2015). NMs can be used in agriculture on a broad spectrum, as well as increasing crop production and improving soil quality.

1.1 What Is Nanotechnology?

Nanotechnology is an exciting interdisciplinary research area. The term 'Nanotechnology' was popularised by Bulovic et al. (2007) and Taniguchi et al. (1974). Nanotechnology is a field of study that aims to create 'stuff' on the scale of atoms and molecules, such as materials and computers. The diameter of a hydrogen atom is ten times that of a nanometre, which is one-billionth of a metre. A human hair is 80,000 nm in diameter on average. Ordinary physical and chemical laws may not apply at such scales. Between the nanoscale and the macroscale, materials' colour, weight, conductivity and reactivity, for example, can differ dramatically. However, just 6 times the mass of steel, carbon 'nanotubes' are 100 times more powerful. The scientist who coined the word nanotechnology, Eric Drexler, has issued a warning about the development of 'highly powerful, extremely dangerous technologies'. Nanotechnology has been lauded for its potential to increase energy efficiency, assist in environmental sanitisation and address significant health issues. It is believed that it can increase production efficiency substantially while lowering costs. Nanotechnology-based goods, according to an engineers, it would be smaller, cheaper, lighter and more durable, and would require less energy and raw materials to manufacture. Nanotechnology has had a major effect on a wide variety of businesses and everyday lives (Gruère et al. 2011; Scott and Chen 2013). NPs are described as particles with a diameter of 1–100 nm, according to the Environmental Protection Agency (EPA). This material is ideal for use in a variety of creative and novel applications that solve social needs and problems due to its small size and properties (Nakache et al. 2000). The future agriculture applications of nanotechnology and NMs, nutrition, disease resistance, delivery of genetic materials and formation of soil structure are discussed in the following sections. NPs have unique properties that enable them to be used in a variety of fields, including electronics, medicine, pharmaceuticals, engineering and agriculture. NPs are materials with a scale of fewer than 100 nm (Thomas et al. 2012).

1.2 What Are NPs?

NPs are a unique type of material having eccentric properties and a broad range of assortments. NPs are thought to serve as a linkage between atomic structures and material extent. Furthermore, because of their high surface-to-mass ratio and their tiny capacity, inorganic NPs have special properties. Gold (Au) and silver (Ag) NMs, among other metallic NPs types, have been developed, which have attracted a lot of attention due to their outstanding success in a number of scientific fields, as well as optics, biosensing and catalysis. Plant extracts are currently being used as inhibitors and blocking agents in the development of NPs, which may be preferable to bacterial synthesis because it eliminates the need for the complex method of culturing and maintaining the cell. Because of their superior catalytic, optical and electrical properties, NPs, especially Ag NPs, have found widespread use in opto-electronics, detection, diagnostics, antimicrobials, catalysis and therapeutics (Sivakumar et al. 2012). Exceptional free-radical hunting, obstruction of carbohydrate digestive enzymes (-Glucosidase and-Amylase), and a development in glucose absorption rate were used to demonstrate the anti-diabetic potential of AgNPs derived from *Tephrosia tinctoria* (Rajaram et al. 2015). Au and Ag NPs have recently been synthesised successfully by utilising the leaf and root extract of *Panax ginseng*, a medicinal herbal plant (Singh et al. 2016). Netala et al. (2016) demonstrated that NM toxicity risks are reduced when NMs are synthesised using biological processes, allowing for biological applications (e.g. agriculture, drug delivery and bio-sensing). Using nanotechnology in agriculture has numerous advantages when it comes to plant disease management and overall development. Micro/macronutrients and nanoformulations containing fertilisers, for example, have increased crop yield while also serving as a biological controlling agent against numerous plant infectious agents when combined and applied to crop development (Keswani et al. 2016). Some NPs, such as magnesium (Mg), titanium oxide (TiO), zinc oxide (ZnO), silicon (Si), and Ag NPs, play a role in indirectly suppressing plant infection by antioxidant/antimicrobial/heavy metal absorption (Rastogi et al. 2019). NPs were divided into biological NPs (as well as fullerenes) and inert NPs (Karthika et al. 2015). Inorganic NPs, such as noble metallic NPs, have recently received a lot of attention because they have a lot of applications in medicine. A general overview of NPs classification is as described below. The properties of Ag metal change drastically when it is decreased to a particle size of 1–100 nm and Ag-NPs are formed. When $AuCl_4$ or another Aurum salt (such as $AuCl_3$) is reduced in the attendance of catalysts or other reducing agents, Au-NPs are formed, resulting in a shift in the noble metal's basic properties on a scale of 1–100 nm. In solution, Au-NPs look burgundy to purplish. They come in a variety of shapes, including spherical rings, nanorods, decahedral, tetrahedral, sub-octahedral triangles, hexagonal, octahedral and icosahedral, among others (Alaqad and Saleh 2016). Ag and Au-NPs are the most widely studied. NPs is also made from metals such as Pb and Cu, non-metals such as Se and heavy metal oxides such as ZnO and SnO_2. Rajan et al. (2016) investigated the antibiotic efficacy of ZnO NPs and discovered that they are effective against pathogenic bacteria. The representative applications for different types of NMs are listed in Table 1.

1.3 Application of Nanotechnology in Agriculture

Natural or manufactured NMs are used in agriculture. Engineered nanomaterials (ENMs) are divided into three categories: combined, inorganic, and organic containing modified surface mud. There are also applications for salts, heavy metal oxides, nanotubes, heavy metals, fullerenes and black carbon. Micelles and liposomes in lipid-based NMs have a high degree of stability. Self-assembling molecules are often used to make protein-based NMs (Puri et al. 2009). The use of engineered natural microorganisms (ENMs) has been shown to improve plant germination and productivity (Servin and White 2016). Many trees are excellent for NM absorption and storage. The cell of plants' interactions with ENMs can guide changes in the expression of plant genes and related biological pathways that can impact plant production and growth. ENMs vary according to the stage of growth, phase and exposure time for various plant species (Panpatte et al. 2016). Applications in agriculture to improve efficiency are illustrated by many nanotechnology

Table 1 Different types of nanomaterials and their applications

Nanomaterials (NMs)	Constituent NPs	Applications	References
Nanofertilisers	Nano Fe/SiO_2	Enhanced maize and barley seedlings shoot length by approximately 20.8% and 8.25%, respectively	Zhao et al. (2017)
	ZnO, TiO_2, MWCNTs, FeO, $ZnFeC_4$-oxide and Hydroxyfullerness	Growth and production of crops with enhanced efficiency of many crop species including spinach, peanut, mungbean, soy, onion, wheat, tomato, wheat, mustard and potato	Shinde et al. (2020), Derbalah et al. (2018)
	Zinc/Boron, generated on the chitosan emulsion NPs by mounting $ZnSO_4$ and H_3BO_3	Enhanced consumption of zinc, chlorophyll elements and coffee's photosynthesis	Wang and Nguyen (2018)
	Nano-zinc and boron	Increase fruit yields and consistency, rises in pH on pomegranate (*Punica granatum*) juice without impacting the properties of any fruit attribute	Shehzad et al. (2018)
	TiO_2	Compared with plant control *Glycine max* L, a beneficial impact on the oil yield, seed and other elements	Rezaei et al. (2015)
	Nano Fe_3O_4	Increase the disponibility of iron and protein in plants, often used for chlorosis treatment	Siva and Benita (2016), Rui et al. (2016)
	TiO_2 and SiO_2	Minimised Cd toxicity and increased development by promoting the ability of antioxidants and preventing translocation of Cd in the *Oryza sativa* plant	Rizwan et al. (2019)
Nanopesticides	ZnO, CuO and Ag-NPs	Symptoms of soil-borne disease and *B. cinerea* in *Prunus domestica* fruits with the grey mold have been eliminated	Malandrakis et al. (2019)
	Ag-NPs	The development of *Xanthomonas axonopodis* pv. malvacearum and *Xanthomonas campestris* pv. campestris in vitro in *Vigna unguiculata* could be inhibited and there were no phytotoxicity	Vanti et al. (2019)

(continued)

Table 1 (continued)

Nanomaterials (NMs)	Constituent NPs	Applications	References
	ZnO	Interruption in *Callosobruchus maculate* larval and pupal growth and development	Malaikozhundan et al. (2017)
Nanofungicides	Al_2O_3 NPs	Treated effectively rot root *Fusarium* in *Solanum lycopersicum* tomato	Shenashen et al. (2017)
	Metallic NPs	Antibacterial and antifungal activity in plants	Slavin et al. (2017)
	AuNPs	Antifungal activity in *Candida albicans*	Aljabali et al. (2018)
	ZnO	Applied to plants in case of fungal phytopathogens, named *Penicillium expansum*, *Aspergillus niger*, *Fusarium oxysporum*, *Botrytis cinerea*, *Alternaria alternate*, etc.	Jamdagni et al. (2018)
	Chitosan/silver combination (Ag@CS NPs)	Efficacious to rice blast triggered by *Pyricularia oryzae*	Pham et al. (2018)
Nanoherbicides	Atrazine nanocapsulation	Reduced root and shoot growth in *B. pilosa* and reduced the operation of photo system II	Sousa et al. (2018)
	2,4-dichlorophenoxyacetic acid (2,4-D)	Rice husk waste was surface adsorbed with 2,4-D to serve as an herbicide nanocarrier. And they demonstrated reversible and improved sorption of 2,4-D which shows their uniqueness to be a strong carrier for herbicide encapsulation	Abigail et al. (2016)
Seed germination	ZnO	Enhanced rice germination and raises length of radical and plumule	Upadhyaya et al. (2017)
	Six metal oxide NPs binary mixtures (TiO_2, Fe_2O_3, CuO, NiO, Co_3O_4 and ZnO)	Improved *Brassica* seed germination	Ko et al. (2017)
	SiO_2	Boost the germination of the seed	Alsaeedi et al. (2018)

approaches. This included nanoformulation for crop protection, detecting nanobiosensor toxicity, genetic alteration of plants by nanodevices, effective diagnosis of disease and the advancement of agrochemicals. The gain of nanoarrays from genetic content and protein supplies in crop designing, drug supply, pathogen detection and environmental control that need to be monitored (McLoughlin 2011; Pandey et al. 2010; Mir et al. 2017). For resisting plant pathogens and for immersive agrochemicals nanofilms, nanofibrous pads and quantum dots (QDs) open up a new opportunity for agriculture and in other sectors. Crop germination and seedling growth were found to be unaffected by QDs at low concentrations. QDs may also be used to check identified physiological processes in plant root systems using live imaging (Das et al. 2015a, b). For their nanofertiliser properties, FeO, TiO_2, urea hydroxyapatite, ZnO, $nSiO_2$ NPs and carbon-based NPs have all been examined (Kottegoda et al. 2017; Subbaiah et al. 2016). Nano ZnO, SiO_2, FeO and TiO_2 are all examples of nanofertilisers. In the last ten years, there has been a comprehensive study of many NPs for metal oxides such as TiO_2, Al_2O_3, CeO_2, ZnO and FeO for agricultural processing. Both micronutrients and fertilisers were found to increase the condition of the soil at the nanoscale (Jose and Radhakrishnan 2018). The use of TiO_2 NPs in soya has shown that the content of nitrate reductase and the absorption of water and the antioxidant process are substantially increased (Kataria et al. 2019). Nano-encapsulated formulations of pesticides require low dosages of pesticides, and therefore human exposure, with limitable side effects, to make them safe to protect crops (Nuruzzaman et al. 2016). The mesoporous silica NPs (MSNPs) were suggested for chemicals and DNA transmission into the isolated plant cells (Yi et al. 2015). *Prunella vulgaris* callus proliferation was also boosted by Au-NPs and Ag-NPs, either singularly or in combination (Faizal et al. 2016). Colonisation and film growth can all be examined with nanofabricated vessels which simulate capillary activity as well as following the xylon-inhabiting bacteria's movement and recolonisation (Jose and Radhakrishnan 2018). The schematic representation of applications of nanotechnology is depicted in Fig. 1.

1.3.1 NMs in Nutrient Addition

The use of nanotechnology to provide nano-sized nutrients for crop production is known as nanonutrition (Mura et al. 2017). The researchers used both biotic and abiotic NPs. Inorganic sources such as salts are used to make the abiotic form of nutrients or NPs, but this is harmful since many of these are not biodegradable. We will make micronutrients and macronutrients more accessible to plants by using nanonutrition. Insect and pest defence using nanotechnology has been used on plants. Nanofertilisers can improve nutrient uptake and aid in the development of more intensive, sustainable agriculture. Weanlings have been given casein micelles as a source of nutrition. Since these particles are cleared in the stomach proteolytically, the animals of farming are not at risk (Day et al. 2015). Akbari and Wu (2016) suggest encapsulating and shedding hydrophobic and hydrophilic bioparticles of the harsh stomach world using canola proteins cruciferin as NPs. In addition, the volume of iron increased in sunflowers by the Fe_3O_4 coated EDTA NPs (Shahrekizad et al. 2015). The growth of peanuts is boosted by an increased supply of iron and iron

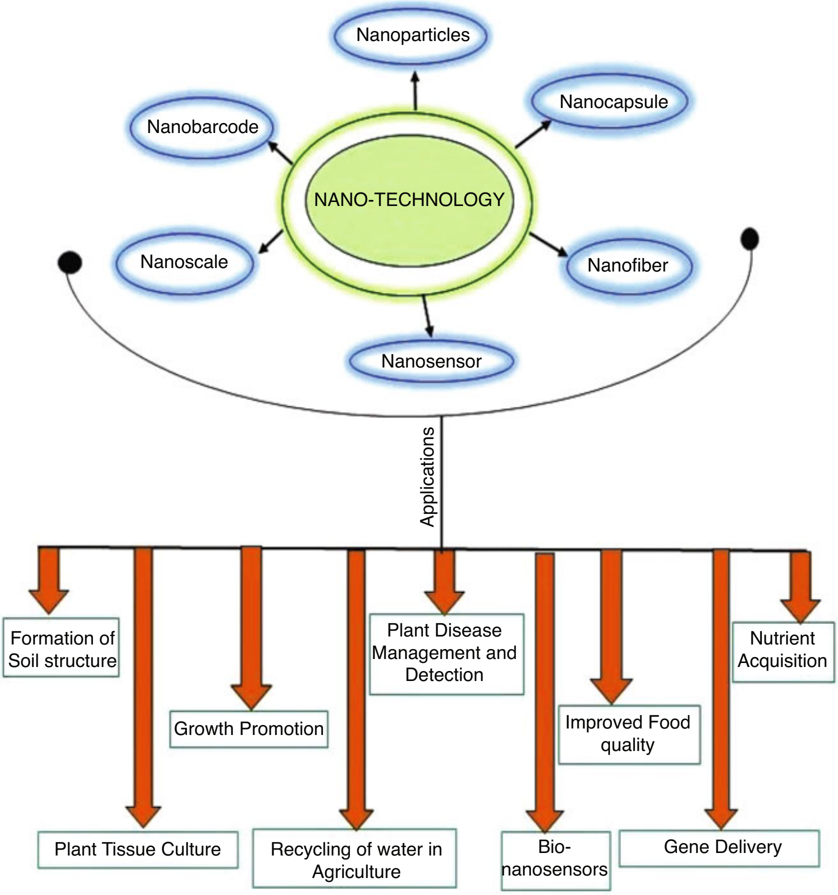

Fig. 1 Various types of nanotechnology applications are using in agriculture

oxide NPs (Rui et al. 2016). The implementation of Zinc-boron nanofertiliser prepared with $ZnSO_4$ loading chitosan NPs emulsion in coffee leaves enhanced Zn, N and P uptake, and improved chlorophyll content (Wang and Nguyen 2018). When exposed to different amounts of Cu-NP, the number of Cu^{+2} ions produced by Cu-NPs did not affect *Phaseolus radiatus* and *Triticum aestivum*. Saharan et al. (2015) demonstrated that CuO-NPs can be used in hydroponic environments, shifted and biotransformed by rice plants, but even Cu-NP is bioavailable. The casparian NPs will pass into the exodermis, epidermis and cortex of the root before reaching the endodermis. Tomatoes' early blight and *Fusarium* wilt may be treated as antifungal agents with Cu-chitosan NPs.

1.3.2 NPs Promote Plant Growth

Researchers worldwide have also researched this growing promotional behaviour of unique metal NPs (Salem et al. 2015). In *Brassica juncea* plants treated with iron sulphide (FeS) NPs, activate RuBisCo small subunit (rubisco S), RuBisCo big subunit (rubisco L), glutamine synthase (GS) and glutamate synthase (GltS). The mechanism by which FeS NPs have caused growth and yield increase is thought to be the carbon and nitrogen assimilation pathways that are activated at various growth stages. Rawat et al. (2017) announced that *Brassica juncea* 7-day seedlings exposed to Ag metal NPs have growth and antioxidant status (at 0, 25, 50, 100, 200 and 400 ppm). Ag NPs treatment improves the fresh weight, root and shoot length and vigour index of seedlings. The treated seedlings had a 32.6% increase in root length and a 13.3% increase in vigour index. ArgovitTM is an *Allium cepa* AgNP formulation. The concentration level for polyvinylpyrrolidone (PvP)–AgNP formulations tested is 10–17 times higher than those formerly announced and has not caused genotoxic or cytotoxic damage to *A. cepa*. (10–1666 g/mL completed formulations). Favour development without damaging roots or bulbs, in other words, low concentration (5 and 10 g/mL) (Francisco et al. 2020). The benefits of nanofertilisers are lower degradation of water bodies, less ground contamination, delayed and constant release of nutrients, an improvement in output yields, better photosynthesis (Mehrazar et al. 2015). Fe_2O_3-NPs rise the content of plant protein and iron to reduce chlorosis disease (Siva and Benita 2016). Hafeez et al. (2015) demonstrated that Copper (Cu-NP) improved wheat cultivar in the Millat-2011 crop and yield by growing chlorophyll content, leaf area and root dried weight and shoot dried weight. Yassen et al. (2017) reported that the SiO_2 nanofertiliser application rises cucumber growth and production by increasing the phosphorus and nitrogen content of the plant. Chitosan is a randomly dispersed polymer, connected to biodegradable and biocompatible N-acetyl-glucosamine units and β-(1,4)-D-glucosamine. Several examples show that chitosan NP application results in impressive plant growth. Nano chitosan-NPK 239 fertiliser enhances the growth and productivity of wheat plants grown in sandy soil (Abdel-Aziz et al. 2016). Chitosan–polymethacrylic acid (PMAA) NP in pea plants increases the build-up of starch at root ends. In addition, protein production such as legumin and vicilin was increased (Khalifa and Hasaneen 2018).

1.3.3 Management and Detection of NMs in a Plant Disease

Appreciating the mechanism of contamination and propagation, and then looking at modes by which this can be alleviated, is the most critical aspect of plant disease management. However, this was a problem until recently when we were able to investigate the intercommunicating use of nanofabrication between plant and disease agents to know better how microbes migrate. By nanomanufacturing the xylem system, we could better appreciate the mechanism of the microbes in the xylem system. Earlier, all such experiments would need tissue damage to produce a good picture of the process. Ag NPs in an investigation performed by Medda et al. (2015) showed an inhibitory influence on fungal germination and budding. In addition to the structural disruption, there have been changes in the sugar, lipid and protein content. *Ralstonia solanacearum* is one of the species affected by Ag (Aravinthan et al. 2015). Antibiotic use must be restricted and monitored, and procedures must be developed under which NPs can effectively prevent the spread of diseases (Huijskens et al. 2016). Studies indicate that heavy metal NPs can lysis negatively loaded membranes of bacteria because of their load (Gahlawat et al. 2016). Such a case was the splitting of the ß-lactam ring with certain microorganism. A ß-Lactam antibiotic containing NPs blocks the tendency of microbes to cleave (Kalita et al. 2016). The biocidal function of the membrane cell wall of bacteria has been established by hydrogels made from NPs such as qPDMAEMA (Xu et al. 2015). Cu-chitosan NP inhibited the growth of *Alternaria solani* and *Fusarium oxysporum* in tomatoes by 70.50 and 73.5%, respectively (Saharan et al. 2015). In the case of *Macrophomina phaseolina*, 25% of ball mouldings are more antifungal in the combination of nanotrifloxystrobin and 50% of tebuconazole (75 WG) fungicide than conventional fungicides (Kumar et al. 2015). Chitosan (CS) and Ag NPs (also called Ag@CS NPs) were antifungal activity in opposition to the rice explosion which was created by *Pyricularia Oryzae* (Pham et al. 2018). The antifungal and antiprotozoal activity of ZnO-NP with ciprofloxacin and ceftazidime were detected in *Aspergillus niger*, *Alternaria alternativeata*, *Penicillium expansum*, *F. oxysporum*, and *Bancroftian filaria*. The maximal antifungal efficacy was reached when 0.25 mg mL^{-1} ZnO-NPs were paired with 8 mg mL^{-1} ciprofloxacin and 32 mg mL^{-1} ceftazidime (Jamdagni et al. 2018). Anti-fungal experiments have been conducted utilising zinc oxide NPs (ZnO-NPs) with results indicating that ZnO-NPs have a significant ability to inhibit the growth of fungal infectious agents (Khan et al. 2019). Arciniegas-Grijalba et al. (2017) have been studied the antifungal impact of ZnO-NP on *Erythricium salmonicolor* pink coffee disease. Two categories of ZnO synthesised at several concentrations have been utilised to quantify inactivation of fungal mycelial formation. High Resolution Optical and Microscopic (HROM) and Transmission Electron Microscopy (TEM) were found to prevent growth and morphologic transformation such as dilution of hyphae fibres and fungal clumbing patterns at 9 mmol L^{-1} zinc acetate ($ZnC_4H_6O_4$). The CuNP-based settlement of *F. culmorum*, *F. équiseti* and *F. oxysporum* has decreased substantially, according to Bramhanwade et al. (2016); *Staphylococcus aureus*, *Escherichia coli* and *Proteus vulgaris* colonisation was studied by Mishra and Sharma (2017) who found that most of them were inhibited by *P. vulgaris* colonisation while *S. aureus* colonisation was least inhibited. Both of these have a minor inhalation effect on colonisation by Ag NPs *Staphylococcus aureus*, *Bacillus cereus*, *Listeria monocytogenes*, *Salmonella typhimurium* and *E. coli* (Patra and Baek 2017). The combined antimicrobial chemicals and Ag-NPs have had a greater inhibitory effect and are known for their antifungal property (Khan et al. 2019).

1.3.4 NPs in Management of Pests

Biopesticides have long been praised as a cleaner alternative to chemical pest control, offering a lower risk to humans and the environment. Natural materials are used in their production, such as animals, trees, bacteria and nematodes. Because of their efficacy, target precision, biodegradability, environmental protection and appropriateness of integrated pesticide control (IPM) programmes, biopesticides are gaining popularity. Biopesticides still account for just 2% of all plant protectants used worldwide, despite an upward trend in growth for the last two decades. Agriculture's use of biopesticides is perfectly matched with industry trends that encourage safe eating while still preserving the environment. Residue-free food is becoming increasingly popular among consumers. The most common insect pest control biopesticides are secondary metabolites, including tannins, polyphenols, glycosides, flavonoids and alkaloids. Examples are *Tagetes*, *Acorus*, *Gnidia*, *Argemone*, *Vitex*, *Ocimum*, *Chrysanthemum*, *Annona*, *Calotropis*, *Neem* and *Toddalia* (Singh et al. 2014). Siva and Kumar (2015) grew Ag NPs taken from *Aristolochia indica* leaf extract. Laboratory biosecurity against *Helicoverpa armigera* III instar larvae demonstrated a rise in the larvae efficacy of antifeedant with lower values of (Lethal Concentration) LC_{50} of 84.56 and 309.98 mg mL^{-1} compared with LC_{50} values of 127.49 and 766.54 mg mL^{-1} or crude aqueous extract. In environmentally safe way, silver and plum NPs are synthesised. *Sitophilus oryzae* pesticide operation with a 100% success rate (Sankar and Abideen 2015). Cotton leafworm larvae are completely eradicated when the CuO-NPs are used, such as *Spodoptera littorals* (Shaker et al. 2016). *Callosobruchus maculatus* larva and pupal development are delayed with *Bacillus thuringiensis* coated ZnO NPs. The Bt-ZnO NPs are effective nanopesticides against *C. maculatus*, according to the study (Malaikozhundan et al. 2017). The different types of nanoagrochemicals, along with their applications, are schematised in Fig. 2.

1.3.5 Nanomaterials Utilised in Plant Tissue Culture

Some of the techniques used to remove microbial infections from explants include somatic embryogenesis, callus induction, somaclonal variation, organogenesis, secondary metabolite and genetic transformation enhancement. These are just a few of the applications for NPs in plant tissue culture. It has been demonstrated that adding ZnO-NPs to the MS medium results in cultures being free of infection (Helaly et al. 2014). In a temporary immersion bioreactor method, Ag-NPs (Agrovit) seemed to have potential hermetic effects on the regeneration of *Vanilla planifolia* (Spinoso-Castillo et al. 2017). *Prunella vulgaris* callus proliferation was also improved by Au-NPs and Ag-NPs, either singly or in mix (Faizal et al. 2016). It has been demonstrated that incorporating Ag-NPs into tobacco can help to reduce the harm caused during protoplast isolation by cellulolytic enzymes (Bansod et al. 2015). It has been demonstrated that increasing the quantity of ZnO-NPs in the MS medium causes *Lilium ledebourii* to accumulate more special bioactive compounds (Chamani et al. 2015).

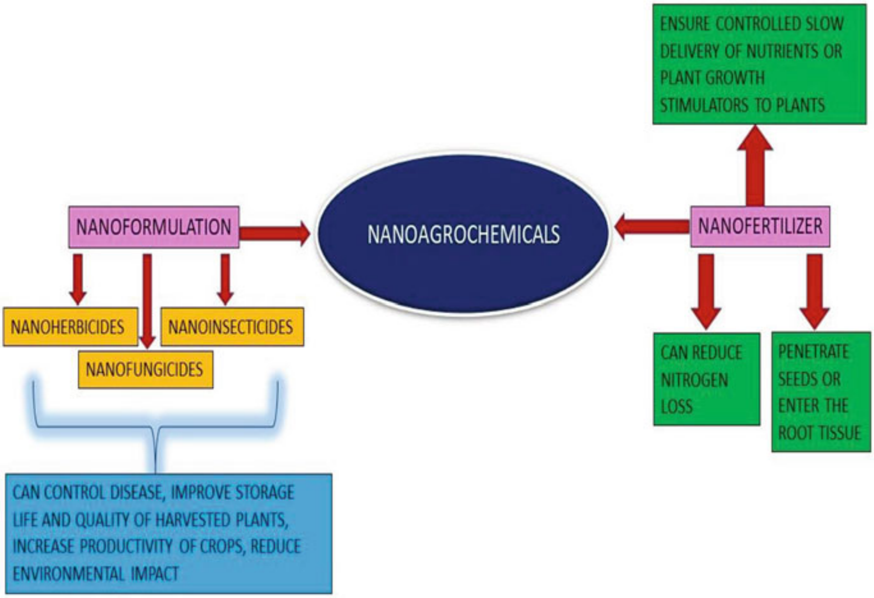

Fig. 2 Types of nanoagrochemicals application

1.3.6 Agricultural Nanotechnologies and Water Recycling

Water is one of the most important and critical elements in agriculture. In agriculture, it is a valuable and expensive commodity. However, the water used for irrigation in most agricultural communities comes from a polluted origin. This contagion could come from any type of waste disposed in the household or in the industry. These infections are detrimental to both the yield and the soil fertility (Fatta-Kassinos et al. 2011). Nanoporous materials, certain membranes and other NMs have recently been used in wastewater treatment as a result of recent nanotechnology implementation (Prasad and Thirugnanasanbandham 2019). The following are some of the approaches that can be used to improve the consistency and protection of water: (1) Biological hazard purification, (2) Pollutant removal and tracking, (3) Wireless nanosensors.

1.3.7 Agricultural Waste Recycling Applications for Nanotechnology

A broad community of researchers is investigating how green technologies can be used to solve current and potential problems. These items must be marketable, ideally and biodegradable. Agricultural waste (AW) can be used to produce green technology-based products (Sangeetha et al. 2017). Over time, the volume of farm waste has increased as a result of the increasing productivity of the agricultural sector. The majority of farm waste is made up of leaves, stems, empty fruit bunches and different plant materials. They contain a lot of lignocellulosic content (Abdul Khalil et al. 2012). Uses have been developed for nanocellulose of cellulosic material derived from industrial waste. In addition to nanocellulose, efforts were made to withdraw noble metals from plant waste for utilisation in medicine supply organisations (Mahal et al. 2013). Au-grape waste NPs are associated with breast cancer cells in humans and are soluble in vitro in cancer inspect (Krishnaswamy et al. 2014).

1.3.8 Nanobiosensor Act as a Biodetector in Soil and Plants

Nanobiosensors are made up of small, transducer-based materials which transmit signals to reconnaissance elements so that a single or multiplex analysed analyte can be detected. These include NMs, QDs, magnetic, carbonaceous and noble metals, signal transduction (electro-chemical, optical and magnetic) and recognition elements (antibodies, aptamers, proteins, and enzymes). Moreover, the recognition elements are further categorised into single analytes metalloids (nutrients, pesticides, soil humidity) and multiplex analytes metalloids (Pb, Hg, Ni, Cr, Cd, Cu, As). These are employed for use for deployment for nanosensor design (microfluidic, optofluidic and substrate/scaffold devices) which is shown in Fig. 3. Fictionalisation, immobilisation and miniaturisation are the intriguing features of nanobiosensors which integrate transduction system biological components into complex architecture to increase NMs' analytical performance (Arduin et al. 2016). The nanobiosensors have an on/off feature, detect analytes in parts per trillion (ppt) and limit the matrix analysed centred on nanoformulation (Antonacci et al. 2018).

The complementary content explains the most commonly used nanobiosensors, their sensing techniques and their use in soil and water systems analysis. Early application of the soil can help prevent adverse effects. Are there considerable health threats due to the concentration of highly toxic metal ions in arable soil and plants beyond thresholds? They are studied using chemical optical sensors that employ electromagnetic radiation as a means of identifying the binding of them with organic immobilised colour in the sample (Gruber et al. 2017). Two popular optical sensors for heavy metal ions in fluvial water or fluorescent soil and superficial dispersal of Raman are improved (SERS) which are designed with biological macromolecules/reduced metal oxides. The use of lightweight nanosensor designs for consumption or commercial use of metal ion detection may be better combined with micro-fluid or paper chip strategy (Ullah et al. 2018).

Urea (most widely used fertiliser for the yield of crops), nitrate, nitrite and urease cause eutrophication and have environmental effects and contaminants in water (Delgadillo-Vargas et al. 2016; Mura et al. 2015). Based on microfluid impedimetric and colorimetric assessments, the detection of these infections in soil and water is done using nanobiosensors. After all, precise and efficient nitrogen compound detection using nanobiosensors offers a spatial and temporal variance in the field of nutrients, allowing for the tracking of their concentration, fertiliser analysis, and

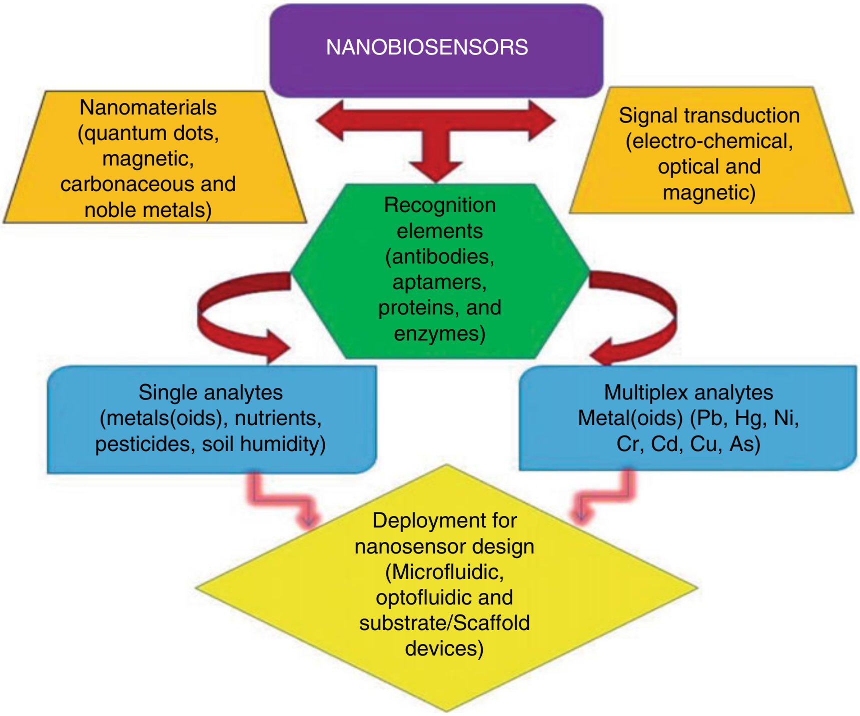

Fig. 3 Types and applications of nanobiosensors

application in smart farming. To calculate the soil's humidity level, nanostructured particles with improved functions such as rapid reaction, sensitivity, stability and the potential to be used repeatedly. Two examples of ceramic-based nanobiosensors with a wide range of sensitivity and reaction include limitable electrodes and graphene oxide (rGO) films for AgPd. By transporting ions and graphene oxide concentration, these sensors take advantage of the attributes of NM and ceramic materials. In inclusion, the NM-based soil quantification biosensor is used for soil analysis in infant stages, and the water solutions for complete organic matter, sodium chloride, organic carbon, residual nitrates and phosphates are restricted only to in vitro conditions (Antonacci et al. 2018). Nanotechnology, known as artificial intelligence technologies and next-generation sensors, has been utilised in robotic nose cones (e-noses). They are widely used in yield field to follow producing methods and plant diseases evaluation, infestation by insects or toxins in soil and water. Although the use of nanotechnologies leads to a new age of intelligent agriculture and minimises associated danger, the widespread use of agricultural and food goods based on NMs and nanosensors that have become less likely to remain in motion has posed concerns about the environment and the health of human beings.

A recent two-year study has shown a useful impact on a microbial and enzymatic community when low levels of nCuO and nZnO (10 mg kg^{-1}) were used (Joko et al. 2017). Denitrification (11-fold increase of NO_3 concentration) was significantly inhibited by another study, and lower levels of nCuO (10 and 100 mg kg^{-1}) would not have a repressive outcome (Zhao et al. 2017). Microbial biomass countervailing results and comfortability of NPs are mostly dictated by the number of NPs applied in the soil. The Ag NPs were found to only harm the activity of microbials by adding a higher dose of Ag to the crop field (Rahmatpour et al. 2017; He et al. 2018). An analytical sensing unit is a biosensor designed exclusively for the evaluation and readability of biological interactions using electromechanical elucidation and transduction. Nanobiosensors containing biofertilisers, including *B. subtilis*, *Pseudomonas fluorescens*, *Rhizobium* sp., *Paenibacillus elgii*, *Azospirillum* sp., and *Azotobacter* sp. encourage crop plant growth under in vitro conditions (Shukla et al. 2015). Enzyme-based electrochemical biosensors were created by mixing enzymatic response and electrochemical methodologies (Vimala et al. 2016). Acetylcholinesterase (AChE) amperometry biosensors are used to detect pesticides and prevent AChE. Xiong et al. (2018) conducted a short report on the advances and issues of organophosphorus pesticide detection in enzyme-functional nanostructure biosensor. A dependable, sensitive, time-saving approach for electrochemical biosensors reduces pre-treatment steps and can be paired with other analytical techniques (Bakirhan et al. 2018). Coal nanotubes (CNTs), which have a particular combination of chemical, electrical, physical and operative properties, can act as scaffolds for the immobilisation of biomolecules on their surfaces, making them suitable for transmitting signals relevant to the study of analytes, biomarkers of disease, or metabolites (Tîlmaciu and Morris 2015). The responsive device of silicon nanofilms (SiNWs) formed by self-assembling (vapour–liquid–solid mechanism) and consistent with the silicon reduction and integration technology of Complementary metal–oxide–semiconductor (CMOS) systems is designed to provide easy and low-cost bacterial sensor supporting hanging bacteria and improving bacterial sensitivities (Borgne et al. 2017). Several fertilisers, herbicides and pesticides may be traced and used in real-time, as well as insecticides, heavy metals, organic contaminants and pathogens (Kumar et al. 2015). Increased pesticide use for various agricultural activities has helped to create breaking sensors to investigate the distinctive chemical and the physical characteristics for pesticide residue detection of NMs. Thus, ‘nanosensors’ are developed for traceability and detection of physicochemical characteristics in otherwise difficult locations and can have higher accuracy, lower limit recognition, selectivity, speed and portability over traditional techniques of identification (Fraceto et al. 2016).

1.3.9 Nanofertilisers Role in Agriculture

Nanofertiliser is a fertiliser made of nanosized molecules coated in a biosensor-coated polymer that releases the particle once the soil is needed. Montreal is the first company to manufacture nanofertilisers successfully. The fertiliser was created by inventing a process for using bacterial enzymes to disassemble the corresponding salts into nanometres. In India, for the first time in the world, a biosynthesis process for producing nanofertiliser was developed for the maintenance of soil-nutrient equilibrium. A nanoparticulate with polymer layer (working as a biosensor) can be used. Types of nanofertiliser are as followed. (a) Nanoporous zeolite, (b) Zinc nanofertilisers, (c) Nanoherbicides, (d) Nanopesticides, (e) Carbon nanotubes, (f) Nanoaptamers and (g) Boron nanofertiliser.

In contrast to chemical fertilisation, nanofertilisers seem to be more convenient. Nanocoating and technologies can assist in several ways to minimise costs and improve efficiency in the form. Soil accumulation, moisture absorption and carbon accumulation are also improved. The word nanotechnology often raises some health and environmental threats and issues. When it comes to danger and protection, only certain places would be pertinent. Initial NM experiments have caused significant risks to health and adverse consequences, even though tissue disruption in the human body affects all essential species.

1.4 Nanopesticides Role in Agriculture

The use of biopesticides is restricted due to their low and environmentally reliant efficacy in the fight against harmful effects of traditional pesticides. Nanopesticides should overcome these disadvantages. Sluggish degradation and controlled release of active substances from suitable NMs will ensure effective pest management for a long period (Chhipa 2017). As a result, nanopesticides are critical for the efficient and healthy management of a variety of pests, and they can help to minimise the use of traditional chemicals and the related environmental risks. To increase their effectiveness, nanopesticides are significantly more effective than traditional pesticides (Kah et al. 2019). Because AI solubility is improved by NPs, the environmental effects are considered to be smaller than conventional insecticides (Kah and Hofmann 2014).

Nanopesticides are not used so much as frequently as regular pesticides. They save money. Their output and lower costs of input by reducing waste and labour often increase pesticide productivity and seed quality. After all, for many reasons, nanopesticides (Ragaei and Sabry 2014) can cause health problems, including those reported by the EPA, the USA as follows:

1. Owing to their incredibly small size, dermal absorption of nanopesticides can pass through cell membranes.
2. By inhaling, they fully go into the lungs and pass to the brain via the blood–brain barrier.
3. The longevity and reactive capacity of certain NMs pose environmental issues and

4. The lack of awareness to quantify the exposure of the atmosphere in engineered NMs.

The findings are reassuring in terms of the staggered extraction of bioactive compounds from numerous crop pests and are valuable instruments for future activities to monitor agricultural pesticides. In recent years, nanosilica has been shown to be effective against insect pests in grain-based outcomes (Gamal 2018). Hashem et al. (2018) have illustrated the red beetle oil (*Tribolium castaneum*) as being of increased strength and stability and concluded that nanoemulsions would mitigate the use of possibly hazardous artificial pesticides to combat insect pests. Weeds are increasingly threatened by urban cultural agriculture. Most nanoherbicides have biodegradable polymers and herbicides' efficacy can be strengthened. Atrazine is depicted by Poly (*ε-caprolactone*), for instance, because of its good physicochemical properties, improved bioavailability and biocompatibility (Abigail and Chidambaram 2017). An analysis of atrazine Foliar's involvement in nanoformulation (*Brassica juncea* L. *Czern.*) plant showed an herbicide-specific interaction through to the leaves' vascular tissues (Bombo et al. 2019). This resulted in a good ability to maintain low herbicide activity concentrations and greatly increase herbicide performance. Similarly, the sleek amaranth (*Amaranthus viridis* L.) was more popular than the hairy beggarticks (*Bidens pilosa* L.) (Sousa et al. 2018). Nanoformulations are thus generated as effective nanoherbicides for treating weeds as depicted in Fig. 4. Herbicides encapsulated in poly (*ε-caprolactone*) are less toxic to *Pseudokirchneriella subcapitata* and *Prochilodus lineatus* than herbicides alone, but they are more toxic to *Daphnia* species (De Andrade et al. 2019). Stringent approaches to risk analysis of nanoparts can be used to characterise the positive forms of molecular and cellular nanopesticides focused on these threats and other studies of NPs (Pandey et al. 2018; Diez-Ortiz et al. 2015; Tiwari et al. 2020).

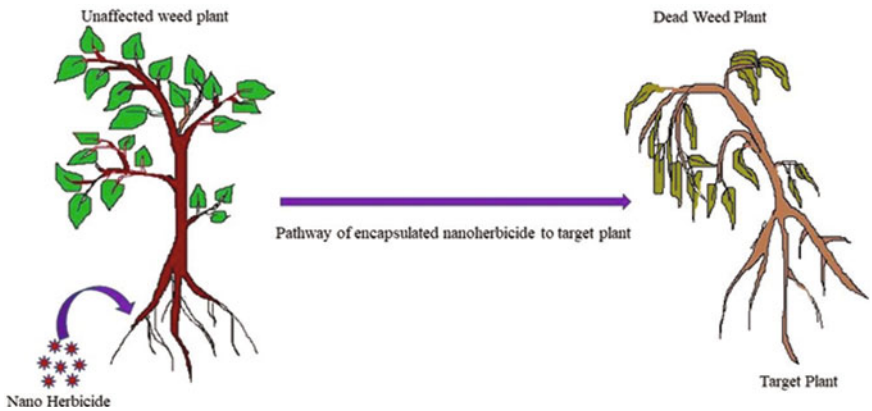

Fig. 4 Effects of nanoherbicides on weed plants

2 NPs-Mediated Gene Delivery

The plant cell wall, which renders genetic manipulation even more elusive in plants than in animal cells, is another major impediment to replacing plants with new and improved traits. Gene of interest transfer in plants can manifest in many ways, along with agrobacterium-mediated transformation, electroporation and biolistic particle transfer (Rivera et al. 2012). While efficient in a variety of plants, these methods possess disadvantages such as reduced plant species productivity, irreversible damage to target tissues and other issues. Tissue culture requires regeneration, which is labour-intensive, as well as the unwelcomed alien genome (Joldersma and Liu 2018). It has a wider range of agricultural research applications, including the use of nanocides to treat plant diseases, enzymatic nanobioprocessing to generate energy from AW, and as a possible gene carrier. NPs, nanofibres and nanocapsules are among the instruments available for gene manipulation (Wang et al. 2016). Methods of gene transmission mediated by NPs have many advantages for transgenic plant development, including passive biomolecule delivery to plants, which is beneficial because it is a minimally invasive, species-independent process, and it allows for plants that have been genetically altered in vivo (Cunningham et al. 2018). Kámán-Tóth et al. (2018) recently developed *Agrobacterium tumefaciens* electroporation which was performed on a direct overnight-grown culture plate and also found to be easy and efficient, minimising the probability of cell injury during the processing of *A. tumefaciens* cells, reducing the number of washing measures and removing the need for a shaking incubator. The observational study of centrophenoxine on *T. aestivum* L. is remarkable, a drug-derived compound that selectively stimulates auxin synthesis and removes the highly corrosive product 2,4-D (Ismagul et al. 2018). By combining the cotton worm's *chitinase* gene with cells bombarded on maize cells, Osman et al. (2015) were able to establish an insecticide-resistant maize plant that was resistant to *Sesamia cretica*, the corn borer. The potential for transformation using biolistic approaches is limitless. A reporter gene, egfp was found in a seasonal liana, *Tripterygium wilfordii* delivered by particle delivery system (PDS)/1000 and had been modified often with hygromycin. The size of the particles, the amount of plasmid DNA used, the helium strain used, and the distance from the cell at which the particles are bombarded are all factors in obtaining high-efficiency (19.17%) transformants (Zhou et al. 2018). They have a higher surface-area-to-volume ratio due to their small size. NP-mediated carrier systems are one of the most significant uses, and due to their unique optical properties, they are still the most popular route for delivering biomolecules, particularly genes, into the host (Karimi et al. 2016). In *alfalfa* plants, Amani et al. (2018) used positively charged polyamidoamine (hPAMAM dendrimer) NMs in combination with transgenic using ultrasound and identified them as genetically transformed plant cells using the *GUS* reporter gene.

3 NPs Identified Environmental Pollutants and Remedy Nanotechnology

On our developed planet, responsive identification and successful elimination of a growing array of chronic and evolving environmental contaminants face significant challenges (Liu et al. 2011). Onsite installations can include sensors, diagnostic and remediation instruments that allow close monitoring of environmental factors. As a result, plant growth and safety, as well as agricultural production, are improved and agrochemicals are decreased in precision agricultural terms. NMs are versatile products in general environmental contamination, identification and remediation techniques. Environmental contamination is one of the world's biggest issues (Das et al. 2015a, b). It is possible that chemical compounds of either natural or anthropogenic origin have polluted the soil and groundwater in sufficient quantities to pose a significant health or climate risk (Thomé et al. 2015). In nanotechnology, these environmental issues relating to soil and water conservation are seen as potentially sustainable solutions. New cost-efficient ways of eliminating soil contaminants like heavy metal/metalloids, dyes and organic pollutants can be contributed by a technique based on nanotechnology, as well as for the treatment of sewage and wastewater. Heavy metal ions and organic molecules have also been removed using metal oxide NPs. Due to its redox cycle, ion exchange, high contaminant affinity and magnetism, iron oxides have already been frequently used as potential adsorbents in the atmospheric. One of the iron oxides (Fe_2O_3), Magnetite (Fe_3O_4), is used for the adsorption of pollutants (Adeleye et al. 2016). Magnetic oxides can be removed via aqueous phase easily after extracting the pollutants, which renders the cleaning process more economical. Bimetallic nanostructures, that is, Pd/Fe, Ag-Fe and Ni-Fe, have finally been formed to solve NP agglomerations with carboxymethyl cellulose, polymers and surfactants stabilised. And hence, these structures have been studied for their right to eliminate and dissolve heavy metals, dyes and halogenated compounds effectively (Li et al. 2016). Heavy metals, especially plumes (Pb^{2+}) and Cd^{2+}, can be irradiated using (Al_2O_3/TiO_2) nanocomposite with brittle Ti silicate (Das et al. 2015a, b).

4 NPs-Mediated Improved Food Quality and Safety

4.1 Nanoemulsions

Nanoemulsions are composed primarily of three main ingredients: a surfactant/emulsifying agent, as well as water and oil. The emulsifier is crucial because it helps not only to bind the ingredients together but also to prevent them from sticking together and reduces the amount of surface energy (interface tension) between the oil and water phases per unit area and also helps the oil and water phases mix better. However, repulsive electrostatic interactions and steric obstacles help to stabilise the nanoemulsion. Nanoemulsions have grown in popularity in recent years as a result of their wide range of applications in various industries. Because of their wide surface area, nanosized emulsions have a major advantage in terms of bioavailability. They can also serve as protective barriers for bioactive materials encapsulated in aqueous media and help lipophilic compounds dissolve better. Nanoemulsions can be divided into three categories: (1) Oil-in-water emulsions (O/W) are a form of an emulsion that combines oil and water, (2) W/O emulsions (water-in-oil) and (3) Nanoemulsions that are bi-continuous. An oregano oil-based nanoemulsion will adequately protect lettuce from *E. coli*, *Salmonella typhimurium* and *Listeria monocytogenes*, according to research (Bhargava et al. 2015). Landry et al. (2015) used carvacrol nanoemulsion to demonstrate the protection of broccoli and radish seed. Mung bean and alfalfa seeds were also protected from the food pathogenic microbes. *E. coli* and *S. typhimurium* are belong to coliform type of bacteria (Landry et al. 2014). In another study on plums, a lemongrass oil-based nanoemulsion was found to protect against *E. coli* and *S. typhimurium* (Kim et al. 2013). A lemongrass nanoemulsion-enhanced sodium alginate film was found to inhibit *E. coli* in one study while also expanding the apple's self-life (Prakash et al. 2018). Biofilm formation is inhibited by a variety of simple oil-based nanoemulsions. Quatrin et al. (2017) demonstrated that *Eucalyptus globulus* essential oil nanoemulsion has been shown to have antifungal properties. It was discovered that essential oil extracted from *Citrus medica* L. var. sarcodactylis supplemented with nanoemulsions were effective against *Staphylococcus aureus* biofilm. Cumin oil nanoemulsion had a similar inhibitory effect on *E. coli* biofilm production and *S. aureus* (Amrutha et al. 2017). When compared to their free form, the anti-biofilm behaviour of essential oils was found to be improved in nanoemulsions (Lou et al. 2017). Two of the primary goals of using nanoemulsions in the food industry are encirclement and distribution of a biologically active substance. In the food industry, nanoemulsions can be used to replace foods with low water solubility, such as-carotene (Gupta et al. 2016). Many experiments have shown that nanoemulsions facilitate the absorption of many encapsulated food supplements. A nanoemulsion of curcumin, in comparison to curcumin in its free form, was simple and fast to absorb (Gupta et al. 2016).

4.2 Nanosensors-Mediated Food Safety

A sensor is a compound device that can react qualitatively or quantitatively to a target. Tiny inorganic molecules, gases, or biomolecules may all be considered physical parameters such as protein; DNA or even full cells may be the target. A biosensor is two different structures comprising a biological substance called a receptor as well as another transducer array. The certain biochemical product inherent resemblance to a generic individual can be a receptor inside a biosensor. The biosensors can be divided, focusing upon the number of atoms utilised, into (a) biosensors based on enzymes, (b) biosensors based on an antibody (immunosensors), (c) aptameric biosensors (aptasensors), (d) peptide-dependent biosensors, (e) natural biosensor premised on receptors and (f) gene-related biosensors (genosensors). In anticipation of health issues, especially in third-world countries, detecting water or food is becoming essential for controlling contaminants. Regrettably, effluent outflow into the atmosphere is currently unregulated. Nanosensors, which range from small molecules to large molecules, open up a modern perspective of pathogen observation and recognition such as poisons, therapeutics and vaccines, heavy metals, biologically active viruses, fungi and bacteria, and organic and volatile compounds. The studies and feedback from scientists all over the world have been extremely beneficial in the diagnosis, nutritional screening and toxin-free ecosystem. Several biosensing techniques to examine the specific physical and chemical properties of NMs have been established, and their ability has improved in both the laboratory and field with the addition of excellent stable receptors of high affinity. The following section recaptures the various forms of pollutants found using different nanotechnologies.

4.2.1 Chemical Contaminant Nanosensors

Synthetic contaminants and substance contamination in the wild is one of the major food and environmental problems in the world. Pesticides, herbicides and insecticides are sources of heavy metal contaminants through industrial anabolic practices, because of unsustainable cultivation and medical overuse of antibiotics and medicines (FAO 2016). Aldehydes, for example, are used as nanosensors (Duan et al. 2019) Biphenyls, hydrazine (Teymoori et al. 2018), hydroquinone (Ren et al. 2018), phenols and derivatives of organic toxic compounds (Ren et al. 2018; Wang et al. 2018; Jigyasa and Rajput 2018), chloropropane (Fang et al. 2019) and 2,4,6-trinitrotoluene (Malik et al. 2019).

4.2.2 Biological Contaminant Nanosensors

Infections of living organisms include disease-causing species like bacteria, viruses and fungi found in raw fruits, vegetables and meat. These pathogens may enter nutrition with drinkable water by faecal pollution, soil contamination, or pests. Bad handling practices can allow these to reach even canned or packaged foods. Numerous factors have been described for combating pathogenic bacteria via its enterotoxins, and they are now being used to detect bacteria as small as single cells. *Salmonella* sp. (Zou et al. 2019), *Escherichia* sp. (Kaur et al. 2017) and *Pseudomonas* sp. (Kaur et al. 2017) are the most common pathogens (Hu et al. 2019).

5 NMs Impact on Soil/Plant System

5.1 Impact of Soil Organic NMs

In modern agriculture, the use of nanotechnology may also have important implications for soil organic matter (SOM) dynamics. However, these impacts can vary according to the quality of the SOM because they can either be hydrophilic or hydrophobic and, because of their biochemical variations, their decomposition in the soil is distinct (Grillo et al. 2015). According to latest research, the mechanics of SOMs are impacted differently depending upon soil properties, test conditions and ENM dosage utilised for the investigations (Rahmatpour et al. 2017; Schlich and Hund-Rinke 2015; Shi et al. 2018). The use of low dose Ag NPs has no major influence on the nature of SOM (Rahmatpour et al. 2017).

Instead, the stabilisation of SOM by the combination of humic molecules using covalent bonds helped other kinds of metal oxides, including TiO_2 NPs, too (Nuzzo et al. 2016). Because of their HS-complexity, Simonin et al. (2015) showed that TiO_2 NPs have no effect on microbial SOM dynamics in most cases; however, they can reduce SOMs by improving their stability. The use of ZnO NPs has reduced the efficiency of littered biodegradation of organic carbon by upto 13% as microbial activities have decreased (Rashid et al. 2017b). Another study found that using Fe_2O_3 NPs reduced CO_2 emissions by upto 30%, demonstrating that the use of nanomaterials in the soil causes fewer SOM to break down (Rashid et al. 2017a). The NMs will protect the environment by releasing CO_2 into the atmosphere through organic emissions, which will help to reduce global warming. Higher CuO concentrations have been linked to lower SOM content in paddy soils, according to Shi et al. (2018).

5.2 Impact of Nanomaterials on Soil Microbes

In comparison to organic NPs, inorganic NPs (silver and metal oxides) have high toxicity, fullerenes and carbon nanotubes since the microbial activity and NP exposure and function vary greatly depending on their type (Rajput et al. 2018; Simonin and Richaume 2015). Gram^{-}ve bacteria, since their cell wall composition is distinct, are also less susceptible to ENM than Gram^{+}ve bacteria (McKee and Filser 2016). The NPs on carbon-based substances were severely affected in C and N cycles by the efficient genes and pathway microbial soil community (Archaea, Bacteria and Eukarya), but S and P cycles are less vulnerable (Wu et al. 2020).

Another analysis found that the soils in microsome were exposed for over 60-days to various doses of the TiO_2 and ZnO NPs, suggesting the reduction of MBC and a negative effect on induced substrate respiration, demonstrating lower microbial activity. In the meantime, the bacterial soil population changed and diversity decreased as a result of these enzymatic NMs (Ge et al. 2011). Similarly, the number of MBC, heterotrophic bacteria and fungi units forming ZnO and Fe_2O_3 NPs has decreased significantly (Rashid et al. 2017a, b). Tong et al. (2016) record marginal effect on MBC and their enzyme activity of C60 NMs of various particle sizes.

Now many NPs (ZnO, Ag, TiO_2, Al_2O_3, CuO, etc.) have a detrimental effect on soil bacterial diversity, as per findings, while Si, Fe, Au, Pb and Ag_2S have either no effect or maybe just mild impact on NP studies (Suresh 2013; Simonin and Richaume 2015; Rajput et al. 2020). Since these consequences are not inherently harmful and may be nonspecific, it is important to take into account the dosage, scale, form and characteristics of NPs and the soil when examining these particles' reactions with regard to the soil ecosystem.

Microbes in the soil can be negatively affected by nanomaterials. The hazard of NPs affects their structure, dosage, concentration and nature, as well as humidity in the soil (Peng et al. 2020; Chen et al. 2019). When NMs reach a certain concentration, they can prevent the growth of certain soil microbes. This has a significant effect on the microbial biomass and population (Kang et al. 2019; Peng et al. 2020). Biogenic NMs have currently been found to be less harmful to soil microbials than their chemically synthesised counterparts and, as a result, they've been promoted as a way to combat intoxication of NPs in soils (Ottoni et al. 2020; Mishra et al. 2020). Given the paucity of data pertaining to biogenic NMs in soils, more research is needed to fully understand their potential.

5.3 Plants Containing NMs

5.3.1 Mechanism for Uptake and Translocation

The pre-optimised application of NPs enhances the germination, stand establishment, growing and development of seeds in several plant species. In addition, NPs convey tolerance to environmental stresses in trees because of the utterance of genes that are resistant to stress (Van Aken 2015) and proteins (Giraldo et al. 2014). The below lines addressed the absorption as well as translocation. NMs in the plant system also define their effect on plant morphology and physiology.

Via a complex chain of events, NPs entering the xylem (vessel), stele and eventually reaching the leaves infiltrate the root epidermis into its cell membrane and cell wall (Tripathi et al. 2017). NPs are integrated into the root zone of plants through apoplastic and/or symplastic pathways and mediated by endocytosis, pore formation, carrier proteins, and plasmodesmata are depicted in Fig. 5. Designed NPs are carried out by numerous lateral root hairs from soil to plant vascular system. The NPs along with water and food particles are transferred to the capillary vascular system of the roots. The NPs are also uptaken by leaves through its different foliar entry by cuticle, stomata, hydathodes, lenticels, wounds and root entry by root tips,

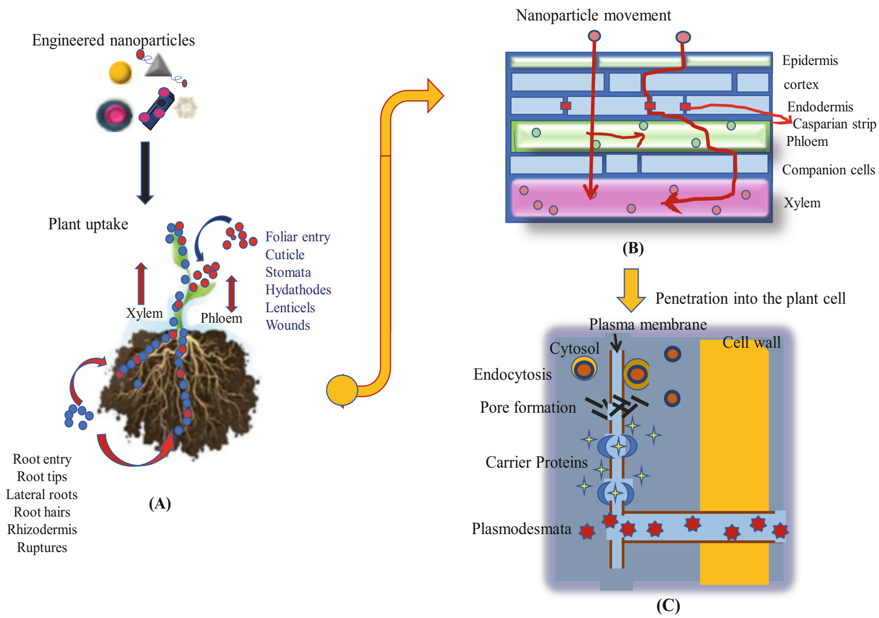

Fig. 5 NPs' uptake and translocation in vascular plants. (**a**) Translocation in whole plant via root to leaves. (**b**) Translocation in tissue by apoplastic and symplastic. (**c**) Transportation in cellular level through plasma membrane

lateral roots, root hairs, rhizodermis and ruptures (Fig. 5a). The NPs penetrate the plant cell; they can be transferred from one cell to another via apoplastic or symplast via plasmodesmata (Fig. 5b). By confining to the carrying proteins, new pores from NMs enter the plant cell via ion channels, aquaporin and endocytosis (Fig. 5c) (Kurepa et al. 2010). NPs entering a cell wall rely on the cell wall's pore size, and smaller NPs quickly move via the cellular wall (Fleischer et al. 1999). Larger NPs, on the other hand, penetrate the stomata and hydathodes (Hossain et al. 2016). NPs are transported utilising pores of the stomata when the particles are 40 nm or larger. Rather than a vascular bundle, these NPs are constructed in storms and are transferred through the phloem to various sections (Tripathi et al. 2017). The NPs join seed coating via parenchymatic intercellular spaces. After all, the fullerene NPs stormed energy pathways and electron transportation (Hossain et al. 2016). The utilisation of NPs has improved the regulation of several genes, such as genes related to stresses and waterways (Tripathi et al. 2017). The *NtLRX1*, *NNtPIP1* and *CycB* genes, which are answerable for transfer of water, cell and cell division task, respectively, were upgraded with the use of MWCNTs (Khodakovskaya et al. 2012). However, at elevated concentrations, technologies can be disruptive. For example, CeO_2 NPs (2000 and 4000 mg) aquaporins regulate the entrance of NPs into the seed coat.

5.3.2 NM Influence on Plants

When NMs have interacted with plants, a variety of morphological modifications occur in plants, based on their concentration and existence (Siddiqui et al. 2015). Consequently, NMs have a beneficial or phytotoxic effect on plants (Siddiqui et al. 2015; Aslani et al. 2014).

Germination, biomass, sheet volume and root elongation are the primary effects of NP toxicity on plant physiological characteristics. NPs can reduce germs, lengthen plants and stimulate the demise of plants (Yang et al. 2017). NPs can reduce germs, photosynthetic rate (Barhoumi et al. 2015), plant growth hormone (Rui et al. 2016) and also cause slow development, changes of sub-cellular metabolism, oxidation to cell membranes (Noori et al. 2020), chromosomal anomalies (Raskar and Laware 2014), water translocation disruption (Martínez-Fernández et al. 2016), alteration of gene transcription pattern (García-Sánchez et al. 2015), and finally, stimulate the demise of plants (Yang et al. 2017). Plant cells and NPs communicate to augment plant gene interpretation and relevant biological routes which then affect plant proliferation and efficiency (Moreno-Olivas et al. 2014). The contacts between plants and NPs can lead to improved plant growth and development expression as well as biological pathways (Moreno-Olivas et al. 2014). They had documented compromising the use of NPs of TiO_2 genomic DNA. Transcriptomic research has shown that the toxicity of NPs disturbed the link between gene regulation upwards and downwards in higher seedlings (Landa et al. 2015). Exposure of the individual wall-mounted carbon nanotubes to *SLR1* and *RTCS* genes in maize was controlled.

5.3.3 NPs Act as Defensing Molecules

The plants species are confronted to metal NPs induce oxidative disruption that leads to the development and activation of the reactive oxygen species (ROS) and antioxidant defence system (Rico et al. 2015). Ascorbate peroxidase (APX), superoxide dismutase (SOD), catalase (CAT), glutathione reductase (GR), guaiacol peroxidase (GPX), and other enzymes and non-enzymatic antioxidants such as glutathione (GSH), ascorbates (ASC), thiols(-SH-) and phenolics furnish antioxidant defensive strategy (Rico et al. 2015; Singh and Lee 2016). The catalysis of superoxide dismutase is used to disperse anion superoxide into hydrogen peroxide (Rico et al. 2015). ROS and hydrogen peroxides have the potential to be used in oxide dismutation. Consequently, these generated ROS radicles can serve as a signalling molecule in activating the plant antioxidant system to decontaminate the free radicles since the application of TiO_2 NPs can trigger photocytotoxicity owing to ROS development (Yin et al. 2012). H_2O_2 to H_2O is reduced by the APX produced by NM ROS (Rico et al. 2015). Plants produced a potential oxidative stress antioxidant attributable to NPs (Wei and Wang 2013). CAT induced in nFe_3O_4, $nCeO_2$, $nMnO_2$ and nAu causes GPX, while $nCeO_2$, and nPt complement SOD. SOD stimulates antioxidant enzymes (Tripathi et al. 2017). In spinach, the application of $nTiO_2$ raised SOD, CAT, APX and GPX. Song et al. (2012) have also documented improved GPX, SOD, and CAT activities. The use of low concentrations (200 mg mL^{-1}), TiO_2, of NPs improved the peroxidase (POD), CAT, SOD, chlorophyll, and malondialdehyde (MDA) of the superoxide by eliminating the ROS and TiO_2 NPs-caused cell membrane disturbance at high concentrations (500 mg mL^{-1}).

5.4 Formation of Soil Structure

The Earth's ecological balance is also most important, and the chemical and biological melting of rocks generates soil, which is a valuable nonrenewable component. The nucleus of a diverse microflora is soil (bacteria, fungi and actinomycetes). It comprises both advantageous and adverse microbes and accounts for approximately up to 75–90% of the biomass in soil. NPs penetrate the natural world by many processes, including the use of NPs, the disposal of nano-related products and urban water smudges that produce NPs (Tolaymat et al. 2017). NPs are both locally produced and engineered in the soil world. In situ, NPs are soil colloids; small and granular fragments which aren't in the nanoscale range play an important role in soil transformation due to cation changes and particle alignment. In addition, weathering allows the creation of NPs, as well as of amorphous rocks, such as Fe and mineral oxides, as a result of soil erosion. The most important man-made sources of NPs are metal oxides (ZnO, CuO, SiO_2) and metal (Zn, Fe, Al, Ag, Ni, Si) (fullerene). Metal NPs, for instance, have been frequently employed and investigated by numerous investigators in connection to microbial diversity and its activities in soil (You et al. 2017).

6 Future Prospects of Nanotechnology

In this part, we have seen the different fields of application of nanotechnology. Nanotechnology may be used in precision agriculture; waste reduction and contamination; improving the use of services such as water, fertilisers and pesticides; and many more. With the advancement of years and new knowledge is incorporated into the world of nanotechnology, the fields where NMs can be used in agriculture can be extended further. The scope of use of the current materials will be improved over the years. The above limitations should then be addressed. As these issues remain unanswered, this technology is being impaired in the agribusiness.

The fields for the use of nanotechnology in the agro-industry are the following:

1. Terms of planning supply systems to be used in fertilisers, pesticides and herbicides application.

2. Nanosensors, which can be used in smart farming through efficient use of water, fertilisers, nutrients, herbicides, etc.
3. Biopolymers in the nanoscale that may be used for disinfecting and neutralising heavy metals and pollutants.
4. To meet the need for a stable and improved efficiency, researchers must examine the synthesis of improved NMs in the areas of configuration, interface chemistry scale and posology, human and environmental aspects.
5. Foodstuffs should be packaged and stored in a smarter way to strengthen their shelf life and product consistency.

In many areas, nanotechnology is in its prime stage; seeing all this modern advancement, it makes clear that it has a wide spectrum, and there will be objections and disapproval towards any new technology in this area, overcoming all of its myths and ethics in its own right. This invention would aid generations of foodstuffs and not just one. Instead of knowing the advantages and efficiency of technology, we are mindful that few activities are at risk. Nanotechnologies in agriculture provide traditional agricultural methods with new resources such as nanofertilisers, nanopesticides and nanosensors.

7 Constraints

Although nanotechnology may be the solution to many of these problems in agriculture to date, more study is also required to solve public and policymakers' questions about the human, ecology and environmental impact of such materials.

Some of the major issues affecting the use of nanotechnology in the farming manufacturing industry are as follows:

- Interactions between non-targets: these NPs can also interfere with non-target cells or surfaces. For example, if NPs are used to treat non-target organisms or even other compounds as an antimicrobial agent, particles may be used in certain cases, with unintentional results (Chaudhary 2017).
- Effects on the air and humans: While there is continuing analysis into the manufacture of new NPs in different sectors, there is insufficient study of the effects of NPs on humans and the climate. However, Mukhopadhyay (2014) said nanotechnology is the way forward because of its enormous ability to be used by the farming sector.
- Cost effect: While this technology is innovative, it is not a cost-effective approach that all farming nations can adopt. Government and Industry sectors have inadequate funding that could restrict the use of this technology. There is also limited funding needed for research in this area.
- Rising awareness: There is a lack of awareness of the application among the general public and policymakers, as well as information on the protection and positive effects of using this programme.

- Regulations concerning ethics: As this is a modern agri-industry medium, legislation must be developed to ensure the observance of all safety protocols and the proper labelling of NM products. Any of the above constraints will prohibit or hinder the use of this technology in the agro-industry.

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Part II
Nanoagriculture

Approaches, Challenges, and Prospects of Nanotechnology for Sustainable Agriculture

Garima Pandey, Smriti Tripathi, Sangeeta Bajpai, and Monika Kamboj

1 Introduction

The growth of agriculture is a necessary aspect of the economic development in nearly all the developing nations. The current status of escalating worldwide population graph is resulting into a decline in the demand–supply ratio of agri-products (Ali et al. 2014; Contado 2015). The amalgamation of nanotechnology and biotechnology in agricultural sector would play an imperative part in increasing the productivity rate with better packaging and processing of agri-products. Nanotechnology is expansively influencing the globe with enormous applications in almost every field, and in last few years, work in the area of agri-sector has skyrocketed (Corradini et al. 2010; Cui et al. 2010; Dhawan et al. 2011). It pervades nearly every region of agri-sector, ranging from soil health, irrigation and filtration management, sensing and monitoring of biological host-molecules, food processing and packaging, and pest, vectors, and rodent management (http://www.nanotec.org.uk/; Fraceto et al. 2016). Nanotechnology constructs nanoscale materials by making changes at the atomic level. The purpose of utilizing nanotechnology in agriculture is to boost the agricultural yield, to curtail the usage of hazardous chemicals, to deal with the loss of nutrients, and pest and vector management. This also involves enhancing the creation and the promotion of nano-based agri-products, their efficiency improvement, and quality and safety assessment of the agricultural goods.

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However, all the nano-based agri-products also bring in risk issues like contamination of air, soil, and water, or threats to plant, human, and animal health, along with them (Gehrke et al. 2015; Gour and Jain 2019). Owing to the poor information, assessment, and management of the risks associated, it is still not apparent how the environmental sustainability of agriculture will be achieved through nanotechnology in future. Over 1300 commercial nanomaterials (NMs), with prospective applications in various fields, are presently available in the market. The synthesis of nanomaterials with precise dimensions, composition, and property has extended their efficient applications in agriculture (Handy et al. 2008; Hegde et al. 2016). Nanomaterials being used in agriculture could be from natural sources or engineered ones synthesized in the laboratories. Nanomaterials are synthesized by the top-down and the bottom-up approaches of synthesis and are generally grouped into organic, inorganic, and composite nanomaterials (such as surface-modified clays). The applications of biologically synthesized nanomaterials pave the way for sustainability in agriculture sector. The biosynthesis of nanomaterials from green reducing agents without consuming high amount of energy and lethal chemicals has engrossed the attention from the researchers globally (Hochella Jr et al. 2019; Joseph and Morrison 2006; Mukhopadhyay 2014).

2 Green Synthesis of Nanomaterial

In recent years, research has been concentrated on evolving innovative environmental means as an alternate to the conventional mode in order to cut the reaction times, refining the degree of pureness of the products, and increasing the reaction yields. These innovative technologies are incrementally taking modern society toward safer and more sustainable practices and are environmentally friendly. It serves the purpose of protecting human health and environment from hazardous waste. Nanotechnology is an emergent branch of science that involves synthesis of nano-sized particles (less than 100 nm) by physical and chemical processes or from natural resources (green approach) as green agents. Nanomaterials possess fabulous physical and chemical properties with ample of applications. The green nanoparticles (NPs) have numerous applications. They play a significant role in the development of novel and effective drugs, catalysts, sensors, pesticides, optics, photo-thermal therapy, and medicine (Narayanan and El-Sayed 2005; Eychmuller 2000; Salata 2004). So, researchers have focused in developing nanomaterials by green methods.

The synthesis of nanomaterials is usually achieved via chemical and physical methods. These traditional methods require the use of extremely toxic, expensive chemicals and are havoc for the ecosystem. As a need of the hour, to reduce the risk of toxicity in the environment from the different chemicals used in the physical and chemical methods, researchers have moved toward more environment-ally friendly process called "green synthesis." Nowadays, green methodology is adopted to integrate the particles at nanoscale in which compounds derived from natural resources such as microbes, animals, and plants are used. Such green tools to produce NMs are cost effective with low waste generation.

Significant rules to be considered for green synthesis at nanoscale (Darroudi et al. 2011) include:

1. Use of the green solvents in the synthesis.
2. Use of an eco-friendly benign reducing agent.
3. Use of a nontoxic stable material.

The natural biodegradable resources such as enzymes, vitamins, bacteria, actinomycetes, yeasts, fungi, algae, plant extracts, and phytochemicals are the common green systems/vehicles utilized to synthesize highly stable, well characterized, and safer nanomaterials instead of the chemical methods (Machado et al. 2013; Huang et al. 2014; Luo et al. 2016). Among these methods, synthesis via plant extracts is beneficial since it lessens the peril of further adulteration by lessening the reaction time and upholding the cell structure (Ajitha et al. 2015). Some of the systems used by researchers to synthesize nanomaterials by green route are described as follows.

2.1 Bacteria-Mediated Green Synthesis

The defense machinery of bacteria plays a crucial route in the biosynthesis of nanoparticles. When the concentration of ions is high, bacterial cells do not survive and are under stress. To overcome this stress, their cell mechanism, that is, enzymes in cell walls, converts toxic and reactive ions into stable nontoxic nanoparticles. The only drawback in this case is that high concentration of nanoparticles can damage the cell structure of bacteria as they require ambient conditions of pH, temperature, and pressure to survive. Also, rate of synthesis is slow. Researchers reported bioreduction of silver ion to bactericidal Ag NPs by using cell-free culture supernatants of psychrophilic bacteria and silver nitrate as precursor (Shivaji et al. 2011). Different bacteria were utilized by researchers (Du et al. 2017; Singh et al. 2016a, b; Wang et al. 2016) to synthesize intracellular or extracellular Ag NPs of different size using silver nitrate as substrate.

2.1.1 Algae-Mediated Green Synthesis

Algae are most primitive, aquatic photoautotrophic, eukaryotic microorganisms. In recent years, they have been explored for synthesis of nanoparticles. Algae belonging to the Class Cyanophyceae (blue green), Chlorophyceae (green algae), Phaeophyceae (brown algae), and Rhodophyceae (red algae) have been used as bio-tools for synthesis of nanoparticles (Khanna et al. 2020). Algae-mediated biosynthesis of nanoparticles is shown in Fig. 1 (Chaudhary et al. 2020). They have the ability to produce nanoparticles by accumulating heavy metals (Castro et al. 2013).

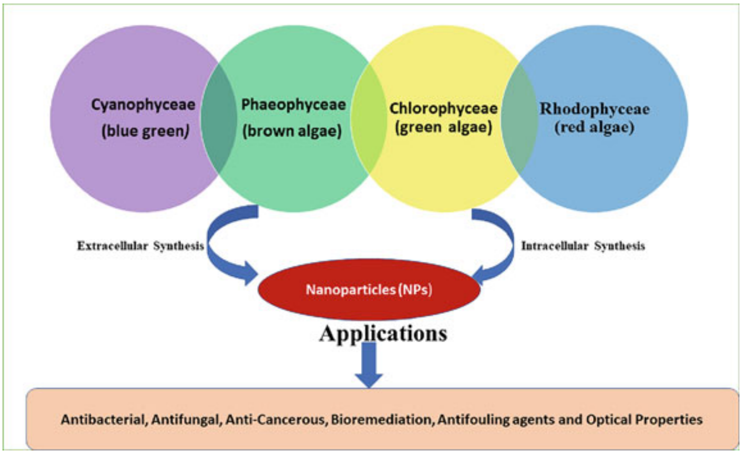

Fig. 1 Algae-mediated biosynthesis of nanoparticles

Cell walls of algae are rich source of bioactive components that make them attractive bio-machinery for the production of diverse nanomaterials by capping and stabilizing the precursors. Brown algae from marine are the rich source of fucoidans, a polysaccharide secreted from their cell walls, utilized for the production of gold nanoparticles (Lirdprapamongkol et al. 2014). Brown algae have the capability to uptake the heavy metals through complex cell walls, laden with mucilaginous polysaccharides and carboxyl groups (Venkatesan et al. 2014). *Chlorella* spp. and *Sargassum* spp. have been expansively reconnoitered for the production of nanoparticles. Singaravelu et al. (2007) synthesized gold nanoparticles from the marine algae *Sargassum wightii* in a short span.

2.1.2 Fungus-Mediated Green Synthesis

Fungus is another widespread bio-machinery to produce nanoparticles as it is easy to handle, affordable, and secretes enzymes that are responsible for synthesis of nanomaterials for mass production. A variety of fungi are being exploited for nanomaterial production due to their ability to tolerate and bio-accumulate the metal. They can withstand laboratory conditions (Fayaz et al. 2011), so have been the first choice of nano scientists for the synthesis of nanoparticles. The active bio-compounds released by the fungus are the bio-tools for production of nanoparticles, which can be controlled to alter the composition, shape, and size of nanomaterial (Menon et al. 2017). Suganya et al. synthesized stable gold nanoparticles by using blue green alga *Spirulina platensis* protein and studied the Au NP potency against the bacterial cell. These gold NPs damage the bacterial cell by penetrating their peptidoglycan layer (Suganya et al. 2015). Extracellular synthesis of metallic nanoparticles is rapid than the intracellular synthesis (Mukherjee et al. 2001; Bhainsa and D’Souza 2006). The major shortcoming of this approach is occurrence of the genetic manipulation of enzymes in fungus recognized for synthesis of metallic NPs (Thakkar et al. 2010). Also, fungus-mediated synthesis process is slow.

2.1.3 Plant-Mediated Green Synthesis

Scientists' community is continually trying to adopt the synthetic route that is eco-friendly and less hazardous to mankind. Based on this strategy, variety of plants and their extracts are being frequently explored recently to synthesize nanoparticles. Plant-mediated green synthesis resulted in stable and less contaminated pure nanoparticles with uniform shape and size. The reaction time was much more reduced (as compared to using bacteria or fungus) without the consumption of toxic reagents. The biosynthesis of NP from plant extract of different plants has been reported (Mohan Kumar et al. 2013; Kuang et al. 2013; Thakur and Karak 2014; Njagi et al. 2010; Wang et al. 2014; Senthil et al. 2012). Mechanism of nanoparticle synthesis involves three stages: activation, growth, and termination (Kalpana-Sastry et al. 2009). Metal ions are reduced to atoms that nucleate to form new entities in the first phase. These new forms will grow to stable NPs in the second phase. Termination stage ends with the formation of NPs of desired shape and size.

2.1.4 Advantages of Green Synthesis Routes of Nanomaterial

Green synthesis routes of nanomaterial have many advantages, including:

- Ease of synthesis and characterization
- Economic viability
- Bioavailability of resources
- Eco-friendliness (Awwad et al. 2020)
- Cost effectiveness
- Environmental sustainability
- Fabrication of nano-objects with controlled size and shape
- Less chances of failure (Garg et al. 2020)

3 Advantages and Usefulness of Nanotechnology in Agriculture

Agriculture is a backbone of economic development for any developing country. The basic challenges that the agriculture industry is facing are: unpredictable weather conditions, industrial development, and biological accumulation, with an increasing food demand due to population explosion (Amin 2018). Global agriculture is facing lots of problems in recent times like lack of nutrients, degradation in soil quality, climate change, reduction in agricultural land area, biomagnifications, limited production of crops, low moisture content in soil, lack of manual labors, and genetically modified crops (the deoxyribonucleic acid [DNA] of which is immune to certain diseases and pests). The escalation in the consumption of chemical fertilizers (from 0.5 to 23 million tons) shows that, till today, we are not overcome from the repercussions of green revolution (Baker et al. 2017; Corsi et al. 2018; Cushen et al. 2012). There is no doubt that the production of our crops has increased manifolds, but it is also true that the amount of required organic nutrients in them has decreased, which has limited the production of some crops. The continuous reliance on uncertain natural factors like climate, soil, and rain in agriculture makes it very unpredictable (Dahabieh et al. 2018; Dayarathne et al. 2019). Consequently, to overcome the obstacle of sustainability, and to fulfill the demands of quality food, it is essential to maintain the database of living and nonliving constituents of the environment (Dudo et al. 2011). To accomplish this, agriculture has to be technically developed and nanotechnology has an important role in it. The promotion of nanotechnology principles in agricultural practices has helped in achieving advanced results. Nanotechnology has immense possibilities and profits in agriculture. When correct amounts of nanoparticles suffuse in plants, it shows so many physical and biological changes in them and indicates quality results in their growth and growth of plants and the rate of seed germination and production (Feregrino-Perez et al. 2018; Hans and Jana 2018). Nanoformulation of insecticides, enhanced crop production via nanocapsules for controlled release of nutrients, pest control through nano-arbitrated genetic transformations, and developing nanobiosensors for site-specific crop management are the few advantages of nanotechnology. The drugs containing nanoparticles deliver its continuous release of nutritional materials, and genes of concern give their continued release through plant cell to improve their absorption, and proliferation of herbicides (Kouhkan et al. 2019).

3.1 Precision Farming

Precision farming is basically an approach to manage the agriculture process with the help of information technology. It makes agricultural practices additionally effective and manageable with regard to crop production and livestock rearing. The main components of precision farming include all artificial intelligence (AI) devices like robotic system, drones, and global positioning system (GPS)-based soil sampling. It also includes sensors, automated means of transport, latest software, and hardware tools. The prime objective of precision farming is to enhance the yield of crops by minimum inputs (Kumar et al. 2015, 2019). Initial technological survey of agricultural land is actually very helpful in precision farming; this survey includes soil quality, and location identification with the aid of technology like sensors, satellite, and computers. Mediation of technology measures all geomorphology accurately—for example, soil quality or required nutrients and moisture in soil and climate—

which can be managed further to enhance and improve quality and quantity of the crop (Kundu et al. 2019).

Precision farming is empowering with modern equipment and technology, like minuscule sensors, that actually helps in supervising soil quality, growth of specific crop, and management of agricultural trash. As reported by the *Forbes*, nanosensors are being used by various countries—for example, R&D Company using nanosensors to monitor sell by date and use by date in stores in Minnesota. Use of nanosensors can optimize the need of chemicals to inhibit the growth of unwanted plants; insecticides and nutritional constituents can be estimated, which can result in maximum farming output in terms of crop production and quality by putting minimum inputs (Liu and Lal 2015). Technological advancement in delivery system and use of nanosensors help in reducing unethical exploitation of agricultural resources like soil, moisture, and soil nutrients. Precision farming with nanotechnology plays a vital role in agriculture by predicting environmental problems like drought and soil moisture as well as detection of seeds and pests, which is very helpful in making agriculture actually sustainable. As soon as the nanosensors understand the edaphic factors, they automatically adjust the irrigation or pesticides. The dispersed nanosensors in the field also understand the existence of microorganisms spread in the fields and then work accordingly. Precision farming plays an important role in managing the farming waste materials and hence is very significant to reduce the environmental pollution at its minimum level (Mabe et al. 2017).

3.2 Delivery of Fertilizers

The continuous use of chemical fertilizers for the purpose of enhancement of production has led to many adverse effects like depleted nutrient level in the soil and degrading of soil quality. Runoff and pollution are also responsible for the great loss of fertilizers. Nanotechnology can help significantly to get rid of these issues with the help of nanoencapsulated fertilizers, as they have been effectively absorbed by the plants, and prevent wastage. The technique of nanoencapsulation has strong control on releasing of nutrients and surface protection (Mani and Mondal 2016). To fulfill the need of potassium, phosphorus, and nitrogen in soil, inorganic supplements like urea and diammonium phosphates are used, which causes squander in economy and environment (Martinho 2018; Milewska-Hendel et al. 2016). The perspective of using nanoencapsulated chemical nutrients is to give the sustainable release and efficient absorption of nutrients by the roots of plants. This is actually effective in reducing the environmental pollution and wastage. These nanoencapsulated supplements seem to be a better substitute for conventional fertilizers.

Various scientific approaches are being applied and studies undertaken to fulfill the requirements of all 22 crucial elements by using nanocomposite materials and nanoclays (Monreal et al. 2016). The fertilizers that are coated with sulphur nanoparticles are used to compensate the amount of sulphur in soil. In this perspective some nanoparticles like kaolin and chitosan have already performed well and give very good results in controlled release of N, P, and K fertilizers. The improved absorption of essential elements from the soil with the help of nanoencapsulation really helped. Protection of plants from various contamination and environmental hazards with upgradation in growth of seeds and roots can be done by using nanosilica or silicon oxide film. To enhance the production of the crop, nonvenomous TiO_2 nanoparticles are being used. Other problems like discharge of water or high rate of dissolving water, denitrification of fertilizers, and sustainable release of fertilizers are being wisely handled by applications of nanomaterials like nanoclays, montmorillonites, zeolites, and bentonites (Morales-Díaz et al. 2017; Mufamadi and Sekhejane 2017; Nasrollahzadeh et al. 2019).

3.3 Nanobiosensors

When nanosensors are arranged with bioreceptors, they collectively form biosensors. These nanobiosensors are very efficient and effective in diagnosis and analysis of atomic-level data of the crop, like detection of pathogens/infections in crop, presence of various chemicals, or moisture content of the soil. Nanobiosensors, made up of antibodies that are encapsulated on fiber optic, can be a good example to sense pathogenic bacteria *Escherichia coli* (Nima et al. 2014). Nanobiosensors are mainly made up of silicon nanoparticles that are fluorescent in nature, and antibodies that are helpful in the detection of various Gram bacteria, for example, *Xanthomonas axonopodis*, which causes severe harm to Solanaceae plants. The specific optical characteristics of Au nanoparticles make them very efficient biosensor for detecting infection, for example the karnal-bunt infection in wheat. Although this is a primary phase of detecting diseases through biosensors, there are many gold biosensors made up of carbon nanotubes (CNTs), nanowires, and silicon nanoparticles that are reported for the diagnosis of plant diseases and pathogens (Nuruzzaman et al. 2016).

3.4 Nanopesticides and Nanoherbicides

Crop production and growth of the plant can be enhanced by developing specific immunity in the plants and by destroying undesirable seeds, grasses, insects, or microorganisms (Ozdemir and Kemerli 2016). However, the excessive use of pesticides could also decrease the process of nitrogen fixation in leguminous plants, and bioaccumulation of pest control chemicals can also deteriorate quality of soil. The application of nanopesticides is really effective and has shown remarkable advantages to overcome these major issues. But the demerit of this process is the frequent runoff and leaching of the soil, which causes major wastage (Pandey 2018a). To resolve this issue, it is essential to encapsulate these pesticides and their sustainable release with increased solubility. Several novel nanoparticles are

Table 1 Outcomes of nanopesticides

S. no.	Nanopesticides	Impacts
1	Ag nanoparticles	Guards oak trees against powdery mildew
2	Hydrophobic nano silica	Controls the spread of *Spodoptera littoralis*
3	Glycol-coated essential-oil-filled polyethylene nanoparticles	Protection of harvest from *Tribolium castaneum*
4	Hydrophobic aluminum silicate nanoparticles as phenolic suspension	Protects *silk worm* from grasserie disease

reported, which are made from silver and titanium oxide, and indicated excellent outcomes to control infection and pest specifically in rice and silkworms (Pandey 2018b). CNTs coated with pesticides, Mancozeb, Zineb, and citric acid have shown remarkable results in controlling the fungal infection. The nanoformulation technique is an efficient method to upgrade the forte and amount of natural constituents. This is obtained because of the anti-pathogenic feature of the nanoparticles and internal immunity of plants (Parisi et al. 2015; Patra and Baek 2017) (Table 1).

Another severe problem that arises in agricultural practice is the growth of weeds along with the crop. Use of herbicides is badly affecting the standing crop and causing deterioration in crop quality and production amount, which is considerably a big loss. Agri-nanotechnology for sustainable agriculture and controlled delivery of herbicides through nanoparticles basically help in proper mixing of herbicides and soil particles, which is very effective in removing the unwanted vegetation without harming the standing crop. Coated nanoparticles are actually very helpful in controlled release and delivery of herbicides in plants. As an example, CNTs containing silver and zinc oxide nanoparticles releasing herbicides containing triazine and ametryn have shown excellent results in controlled release of these herbicides (Prasad et al. 2016, 2017).

3.5 Nanofiltration in Agriculture

Water scarcity is the major problem of agricultural practice at global level. To manage this, development of pocket-friendly equipment and innovative means of irrigation is required, and to cure the water wastage, changing conventional irrigation techniques is needed, although these changes cannot be made in those areas where continual water scarcity is found. Nanotechnology can be helpful in giving rise to solution of this problem; nanosensors give the details about the availability of water in the soil. The use nanofilters is also an effective way to conserve waste water of irrigation with the help of water treatment process (Quist-Jensen et al. 2015). The nanofilters are very useful for removal of hardness and waste water treatment, having dimensions of 0.5–1 nm. It is also suggested that the water used for irrigation should not contain larger particles (>50 μm), heavy metals, or poisonous substances, and must have stumpy salt concentration (Rai et al. 2018). So, it is essential to remove all unwanted substances from the water that is to be used for the purpose of irrigation. The lower quality of water used for irrigation may cause decrease in quality and quantity of the crop. In some countries, where the climate is hot and dry, solar-powered nanofilters have given amazing results. They are found very effective to manage removal of salts from water that is used for irrigation. Application of nanofilters has also shown remarkable enhancement in crop production with the reduction in the demand of fertilizers and irrigation (about 25%) (Raliya and Tarafdar 2014).

3.6 Micronutrient Supply

Although the micronutrients are required in a very small quantity, that is, 100 ppm, they play very significant role in plant physiology. These micronutrients act as activators with so many enzymes. The measured release of important growth hormones of plants has also been observed in chitosan nanoparticles, for example, release of 1-naphthylacetic acid (Rienzie et al. 2019). Nanoparticles of iron oxide when directly applied have shown progressive impact on plant growth. These plants are rich in calcium and their pH value is also high. Nanoparticles containing iron enhanced crop production, protein level, and their weight (Rossi et al. 2014). The dearth of iron in soyabean can also be compensated by an application of nanoemulsion of iron. The presence of micronutrients like Mn, Fe, Cu, B, Zn, and Mo is an essential component of plant growth (Saharan et al. 2013). During the Green Revolution, the drastic increase in the production of crops resulted in a big variation in the concentration of micronutrients in the soil. To compensate the concentration of these micronutrients, nanoformulations of these micronutrients are provided, either through infusion or through spraying on the plants. Nanotechnology actually helps in developing smart seeds by the action of nanoemulsion; these smart seeds are programmed seeds that will germinate only in favorable conditions (Schmid and Stoeger 2016; Sekhon 2014). Smart seeds have very unique properties, like they are capable enough to detect water availability and favorable conditions for their germination and growth. The use of nanosilicon dioxide when applied with SiO_2 in tomato plants has also shown excellent results in germination (Sertova 2015).

3.7 Nanogenetic Changes in Agricultural Crops

Nanotechnology proposes groundbreaking ideas of genetic changes in plants with the help of nanofibers/nanocapsules or nanoparticles. These nano-tools act as a supplier and grasp plant gene and materials regulating the movement of genes. The application of nanofibers in crop modulation, drug supply, and environment

Table 2 Merits of nanoformulation over traditional formulation

Preferable characteristics	Specimens of nanofertilizers
Formulations with the characteristics of sustained release	Nanoformulations are able to manage smartly the dispersion rate of nutrients as per need of the crop
Regulation on distribution and solubility of micronutrients	Micronutrients on nanoformulations increase their solubility and help in disseminating insoluble micronutrients in the soil
Novel methodology for sustained release	Encapsulation of fertilizers through polymer coating specifically monitors the release of nutrients and time intervals
Effective release of nutrients	Nanoformulation potentially increases the time period and efficiency of fertilizers
Percolation of nutrients	Nanoformulation effectively controls and minimizes the loss of nutrients from the soil

impact analysis is widely appreciated. Silicon nanoparticles (mesoporous) have been known for an effective method to transport distant DNA into plant cell (Shweta et al. 2016; Corsi et al. 2018). It has also been reported that nanoparticles that are made up of starch are very efficient in holding and transferring of genetic stuff through cell wall of the plant cell. Nanobiosensors are also playing an important role by noticing the dispersion of pollen grain impurities that arise from modified crops. The merger of nanotechnology and biotechnology has given an amazing way of developing three-dimensional (3D) molecular structure of synthetic DNA sequence as a crystal. The above method can be used to upgrade the crop production by linking and categorizing desired necessary organic compounds like carbohydrates, lipids, and protein fragments to these DNA crystals (Corsi et al. 2018). The agrochemicals encapsulated in nanoparticles are helpful in target-specific sustained delivery of these compounds. They are actually working as a gene gun and giving effective results (Siddiqui et al. 2015; Singh et al. 2018a, b). For example, mesoporous nanosilica and gold-capped NPs have shown excellent result in introducing particular DNA-strands to tobacco and corn plants (Table 2).

3.8 Nanotechnology in Seed Treatment

Seed treatment through nanotechnology gives upgradation in the number and weight of seeds along with weather resistance. This treatment gives about 75% enhancement in dry mass, greater than 15% enhancement in shelf-life, and around 85% enhancement in drought resistance. It has also been observed that there is a threefold increase in vitamin level when they are treated with nanosolutions. This amazingly improves productivity and hence increases revenue (Sozer and Kokini 2009; Subramanyam and Siva 2016; Sun-Waterhouse and Waterhouse 2016).

3.9 Diagnosis of Disease and Pest

Introduction of pest, contaminants, microorganisms, and diseases has led to great harm to agricultural business. The biosensors are extremely useful in the exact and specific detection of such hazards. These biosensors are an efficient tool to make agricultural practice healthier, by averting the occurrence of pests, contagions, and diseases, along with better surveillance of soil health, which automatically results in enhanced productivity and nutrients of food grains (Wakeil et al. 2017; Wang et al. 2017).

3.10 Reinforced Supply of Nutrients and Phytosanitary Products

The novel delivery system in accordance with nanotechnology helps in attaining nutrients and sustained protection of goods, resulting into the upgradation in the quality, magnitude, and the resilience of agricultural products (Wang et al. 2019; Yan et al. 2019) (Fig. 2).

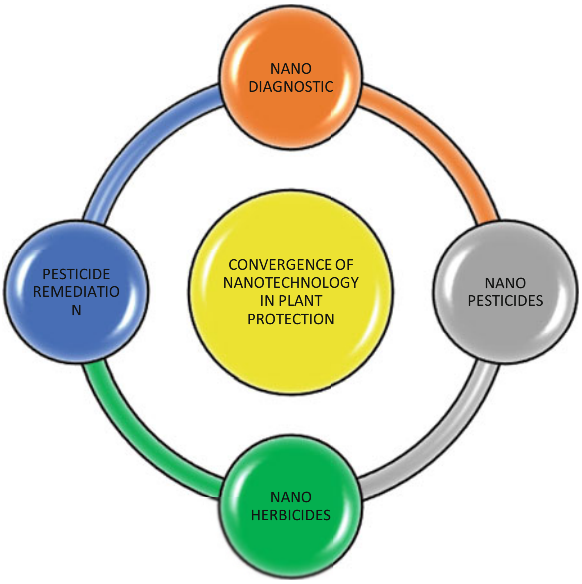

Fig. 2 Nanotechnology in crop protection

3.11 Ecological Aspects of Nanotechnology and Agro-Industry

3.11.1 Viable Use of Water

One of the biggest merits of nanotechnology is seen in desiccated and dry areas, as lesser water availability leads to great damage to the crop production and economy in these areas. The application of nanohydrogels might check the water consumption and enhance the sustainability of crops by controlled absorption of essential nutrients and water (Sozer and Kokini 2009). It has been reported that soil loaded with nanosilver-coated hydrogels is capable to hold 7.5% more water as compared to the normal soil, and hydrogels have shown capacity to store 150 times more water than their weight.

3.11.2 Reduced Pollution and Runoff

Applications of nanotechnology in agricultural practices are extremely helpful in decreasing pollution caused due to chemical fertilizers and treatment practices, and play a significant role in remediation of heavy metals that pollute the soil. This makes possible the use of soil again. Nanosolutions compensate the amount of agrochemicals that have been lost by leaching and runoff and thus effectively conserve the economic loss as well (Yang et al. 2017; Zhang et al. 2016).

4 Agriculture Scenario in India

Indian agriculture is facing an extensive challenge in terms of climatic change, nutrient deficiency, dwindling of cultivable land, stagnancy in crop yield, declining water availability and organic matter in soil, and paucity of manual labor (Pandey 2020).

- The Indian agriculture is still under distress of the fatigue caused by the practices of the Green Revolution. The fertilizer consumption has observed an exponential rise of around four times in the last 50 years of Indian agriculture.
- The existing proportion of 10:2.7:1 for nitrogen, phosphorus, and potassium in India is far off the ideal quotient of 4:2:1. This excessive and unwarranted fertilization is worsening the soil vigor and is an issue of serious concern (Pandey and Jain 2020).
- The extent of nutrient loss is constantly increasing the percentage crop deficit of about 25–30% with every year. In order to sustain the vigor and health of the soil, it is vital to maintain a balanced use of inorganic and organic nutrients; however, the decline in the accessibility of organic nutrients and the subsidy given to the inorganic ones are making it hard to accomplish. Drastic disparities in

meteorological conditions—for instance, the unexpected surge in temperature leading to intermittent droughts, unpredictable rainfalls, thinning of polar icecaps due to global warming, etc.—are additional causes to introduce and adapt alternative approaches in the agri-sector (Pandey 2018c; Prasanna 2007).

5 Challenges

The challenges connected to the sustainable use of nanoparticles for agri-practices are mainly because of the associated health and environmental risks, their co-contamination, and toxicity issues (Yashveer et al. 2014; Singh et al. 2018a, b). The general characteristics and the hazards linked with the usage of nanoparticles are evaluated from the data available in various published articles. The human beings, animals, plants, and the environmental components get the exposure to nanomaterials at some stage during their production, handling, disposal, and managing of the products containing nanoparticles (Sahoo et al. 2021; https://www.azonano.com/article.aspx?ArticleID=5647). The remarkable characteristics of nanoparticles are generally related to their synthesis routes. The chemical composition, tiny dimensions, and shape-effects of nanoparticles are the key reasons to their toxicity that lead to the aggregation and translocation of nanoparticles inside the body causing organ dysfunctions, organ damage, asthmatic attacks, carcinogenic effects, organ enlargements, irreversible oxidative stress, etc. (Singh et al. 2021; Sivarethinamohan and Sujatha 2021; Aamir Iqbal 2020).

6 Future Perspectives

Sustainable agriculture is a coordinated balance between the biotic and abiotic components of agricultural ecosystem for attaining energy balance with the stability of food chains. Nanotechnology has an optimistic prospect for implementing positive changes in the agri-sector to achieve this balance. The applications of nanotechnology certainly can offer inventive and economical solutions and alternatives for enhancing the soil fertility, crop production, pest management, irrigation, and processing and packaging of agricultural products (Seleiman et al. 2021; Chhipa 2016). New skills, specializations, and procedural transformations based on the principles of nanotechnology and increased use of nanochemicals, along with the support, guidance, and regulations from the government, will lead to sustainable growth of agricultural sector. The trailblazing advances in the field of nanotechnology are creating new developments for the reformation of the agricultural sector. Nanosensors have the capability of sensing the pathogens at very low percentage levels (Usman et al. 2020). Nanotechnology provides solutions for converting hazardous and tenacious chemical substances into their harmless or negligibly harmful forms and at times into some advantageous components to be useful to agriculture. Further exploration is needed to reconnoiter in what ways the nanotechnology could aid the nutritional value and the production rate of the crop along with augmenting the nutrient-absorption capacity of soil by using nanofertilizers (He et al. 2019). Further research is necessary in the areas of energy requirement and energy production, crop production, disease diagnosis, detection and control of pollutants from water and soil, protection and packing of food, nutrient supply, and environment management to achieve high and quality yield by effectively using the available resources without altering the environmental sustainability.

7 Conclusion

Agriculture sector being the lone provider of food for all the living beings should necessarily make use of nanotechnology to meet the surging demand of growing population. Nanotechnology has been established as an adept technique to sustainably manage agricultural resources, for the precise delivery of nutrients and drugs to the plants, and for sustaining the fertility of soil. Despite a lot of information in the published articles and patents, still the accurate toxicity information of numerous nanoparticles is unknown and imperceptible. This lacuna in the knowledge, statistics, risk assessment, and management is restraining their wide acceptance and applications. Therefore, it is very much necessary to develop an all-inclusive database, legislations, regulatory policies, and alarm system, along with global cooperation, for successful exploitation of this technology to achieve sustainability in agriculture sector. Nanotechnology in the field of agriculture may still take years to advance from the laboratory to the land, and to achieve this, funds, plans, and support should be provided for this buoyant field to flourish.

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Nanotechnology in Pesticide Management

Maria del Pilar Rodriguez-Torres

1 Nanotechnology in Agriculture

The advancing control in the size of materials that we can study and manipulate has allowed the evolution of science and technology to the so-called nanoscience and nanotechnology and with it the use of the prefix "nano" to referring to all those materials, structures, and molecules at nanoscale (10^{-9} units). The standard ISO/TS 80004-1 for nanotechnology vocabulary determines that the length range in the definition of nanoscale is approximately from 1 nm to 100 nm. In the case of fullerene molecules (dimensions below 1 nm) and single-layer planar structures (e.g., graphene), these are nanomaterials because they are important building blocks for nanotechnology (ISO/TS 80004-1:2015). Given the ratio of surface area to volume in nanomaterials, their interaction with the environment or with other materials or organisms is more effective. Consequently, the amount of nanomaterial required for a given purpose will be less than its bulk counterpart. However, this same interaction confers on it potentially toxic effects and, therefore, a risk to human health and other living organisms. The study of the nanomaterials major part of the time involves multidisciplinary areas of science like physics, chemistry, biology, or health medical sciences, and their application through nanotechnology. This has allowed application in diverse areas as well such as biomedicine, electronics, energy, environment, textiles, or food and agriculture (Liu et al. 2013).

Agriculture has become a fruitful niche for materials at the nanoscale, namely, in the form of fertilizers, pesticides, and nano biosensors for rapid detection of phyto-pathogen and other biotic and abiotic stresses, as well as for the detection of traces of

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fertilizers. Also, these nanomaterials can be used for genetic modification. This chapter is devoted to covering aspects related to nanotechnology potentially applied to agriculture like applications, types of nanomaterials under investigation, regulations, and the like.

2 Nanotechnology and Agriculture

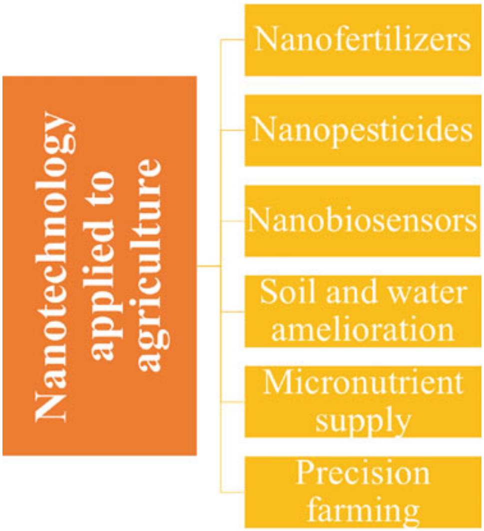
Nanotechnology has entered the scenario of agriculture because it can aid greatly in various manners (Shukla et al. 2019), as shown in Fig. 1. As it can be observed, there are several possibilities for nanotechnology to be applied, although this chapter will focus only on those related to pest management.

In relation to regulatory aspects, the following needs to be taken into consideration (Acharya and Pal 2020):

- Impact of nanotechnology on human health and animal protection
- Environmental effects
- General regulation on the use of nanotechnology worldwide and by country
- Genetic nanotechnology: combination of genetics with nanotechnology to manipulate crops (gene delivery)

In the end, the development of nanomaterials that could be applied to agriculture is still under study in laboratories due mainly to the fact that toxicity in any of its forms (genotoxicity, cytotoxicity, and so on) and its mechanisms have not been well elucidated yet.

Fig. 1 Schematics of the application of nanotechnology in agriculture



3 Pesticides Nanoformulations

The definition of pesticides given by the Food and Agriculture Organization (FAO) of the United Nations refers to all insecticide products, fungicides, herbicides, disinfectants, and any substance or mixture of substances that are used to prevent, destroy, or control any pest type that causes damage or interferes in the production, process, storage, and transport or marketing of food or product of agriculture. The role that pesticides play is highly relevant to guaranteeing the supply of the growing demand for agricultural products and thus meeting the food needs of the growing world population.

The use of traditional pesticides worldwide has increased from around 2 million in 1990 to 4 million tons in 2018 (Lakzian et al. 2019). It is very likely that the increase will not stop due to global demand for food to support the projected population of about 9.7 billion by 2050 (Lakzian et al. 2019). Despite its increasing use with the aim of increasing production, it is estimated that the losses in food production due to diseases, insects, and weeds are about 220 billion (units). The reality is that the activity of pesticides on unwanted organisms has an adverse effect on both the environment and humans, since their use does not rationalize between the different biological organisms on which it has an effect, thus affecting other types of microorganisms that are beneficial for plant growth, reducing counterproductively the production and its quality (Carvalho 2017). An experiment conducted by Ani et al. (Al-Ani et al. 2019) showed that the addition of herbicides (Glyset I.P.A., Glyphosate 48%) and insecticides Miraj (Alphacypermethrin 10%) and Malathion (50% WP) added separately to the soil at different concentrations decreased the microbial activities and counts of soil bacteria, fungi, and actinomycetes. By other side, the pesticide residues negatively affect the soil, water, and the atmosphere. There is a well-known fact that a mere 0.1% of the applied pesticide is effective on its target, and therefore the remaining chemicals remain in the soil where they accumulate as pesticide residues.

Engineered nanomaterials (ENMs) emerge as possible solution to make improvements in seeds and increase their growth rate as well as resistance to stress, and even program them to be resistant to various types of pests. Regarding ENMs as nanopesticides, their application has shown an increase in crop productivity coupled with a reduction in the amount of the active ingredient. These benefits are because, with the use of nanopesticides, the active ingredients can be directed toward the target through various mechanisms at different stages of production. One of the biggest problems encountered during the development of nanopesticides is the lack of solubility in water, to which nanoformulations has a significant contribution in achieving water solubility for insoluble drugs (Mustafa and Hussein 2020).

Some examples of nanoformulations are nanoemulsions, nanocapsules with polymers, and inorganic engineered nanoparticles (NPs: metals, metal oxides, and nanoclays). A novel delivery system was designed for post-loading a biopesticide onto mesoporous silica nanoparticles (MeSiNPs) functionalized with polyethylenimine (bPEI), which is rich in nitrogen. A burst-release behavior was first observed by the nanocarrier MeSiNPs@bPEI after loading it with citriodiol biopesticide (Plohl et al. 2021).

Considering the great variety of existing insects and insect parasitic nematodes, it is favorable to understand the interaction of the various types of nanoformulations and their mode of action in the body of insects. For example, there is evidence suggesting that nanoparticles stimulate the immune system by disrupting bodily functions by producing reactive oxygen species, and that the nature of their physicochemical properties influences their mode of action. The understanding of their mechanisms at an organismal level is crucial in determining their safety for use on nontarget organisms—especially concerning their genotoxicity (Shahzad et al. 2018). From the point of view of economic impact, it is necessary to visualize the framework through which the development and improvement of nanoformulations must be addressed.

Nematodes are multicellular insects with smooth, unsegmented bodies and are very abundant. The species that feed on plants are so small that a microscope is needed to see them (van den Hoogen et al. 2020). During the growth stage of plants, these represent one of the greatest threats to agriculture. Global crop losses from these species are estimated to be in the trillions of dollars. The most recurrent figure presented in the literature is 125 billion dollars (Mesa-Valle et al. 2020) referring to publications from 2003 (Chitwood 2003). Another report in 2021 showed annual losses for 157 billion (Feyisa 2021) (currency not specified). Considering not only nematodes but also other insect species, the potential cost for losses is about 540 billion US dollars per year according to Royal Botanic Gardens, Kewn 2017 report. In 2016, Panini et al. reported a comprehensive study dedicated to calculating the total potential cost of the impact of the 1300 known species of invasive pests and pathogens in around 124 countries in the world (Paini et al. 2016). This study revealed that the existence of invasive pests must be helped by international cooperation to halt their spread. Knowing the economic impact by region, hence, it is required a simultaneous action in the development and improvement of new technologies of nanoformulations for a strategic combat of pests.

Nanoparticles offer to reduce the amount of pesticide used and optimize its effectiveness with a controlled release of its active ingredients and thus reduce the negative environmental impact. However, due to the complex structure of its constituents, they do not degrade immediately and can still represent an environmental and health risk, especially considering that due to the size of the particle they could even be more toxic compared to their traditional equivalent. In this sense, it is imperative to determine the toxicity of the nanoparticles and have in-depth understanding of their effect on human health, for example through the food chain (Rajput et al. 2020). Alternatively, other routes for the elimination of toxic compounds must be addressed. A bioremediation process has been proposed in which bacteria such as *Bacillus*, *Pseudomonas*, *Flavobacterium*, *Sphingomonas*, *Brevibacterium*, and *Burkholderia* use certain chemical groups as their only carbon and nitrogen source, thereby converting the remaining toxic compounds from nanopesticides to nontoxic end-products (Ramadass and Thiagarajan 2017). Other approaches such as the use of nanoparticles based on a stable protein showed an efficient degradation by a proteolytic enzyme that is found generally in the midguts of insects. This opens new possibilities for a more sustainable release of repellents and insecticides (Camara et al. 2019). By other side, the use of nanoencapsulation has offered an alternative to mitigate the toxic effects of traditional pesticides as bifenthrin, which is well known for its detrimental effect on aquatic biota (Blewett et al. 2019). Other approaches have been comprehensively reviewed by Nehra et al., exploring the state-of-the-art development of nanobiotechnology-assisted pesticide formulations that provide a high efficacy with a low risk of side effects (Nehra 2021).

Regulatory
Although pesticide nanoformulations offer enormous advantages over traditional formulations, being a technology still in development, there is an opportunity to have a simultaneous advance in terms of regulations for their use and waste management, based on possible toxic effects on the environment and human health. However, there is still little understanding of the risks associated with the use of formulations in their nano presentation and consequently still poor regulations over its use. The Food and Agriculture Organization (FAO) of the United Nations agrees that science behind the nanotechnology-derived products is still emergent and in continuous evolution. With this growth new issues have emerged, and it is crucial that organizations like FAO and OMS keep aware with the new developments to be in condition to act according to their implications. The FAO and the World Health organization (WHO) experts worldwide have met and published several technical papers covering topics as applications of nanotechnologies, risk evaluation and management of nanotechnologies, and applications of nanotechnologies and their potential food safety implications (Lakzian et al. 2019). The most recent document/ report from FAO/WHO meetings regarding these topics is from 2013 (Meeting WHO and Residues 2007) in which it revised the national and international activities on the risk analysis of nanomaterials (including nanopesticides) in the food and agriculture sectors carried out since the meeting four years before.

The European Commission on the other hand, with the aim to keep European agriculture competitive in the global market, in 2013 brought together scientific experts and key stakeholders for a workshop to review the state-of-the-art research and development into nanotechnology for the agricultural sector. The workshop also focused on possible markets and possible commercial products. A consensus was reached regarding the developments in assessment of nanotechnology and regulations under the European framework. Test methods prior to that date were not accurate enough for nano-sizing given the nano definition. A report from that workshop was published in 2014 (Rauscher et al. 2014) and no workshops nor reports from the last five years were found from the European Commission. The adoption of nanotechnology in agriculture is being regulated in different ways around the word resulting in different approaches to regulate nano-based products. It is possible that risk assessment and authorization of new pesticides with nanoforms or nanoencapsulated active substances will necessitate a separate classification and examination of the products on an individual case basis, to assess the safety of ENMs as active substances. A high level of protection for humans and the environment is only possible by working together with the global community, enabling the development of new helpful products, and promoting their global market (Amenta et al. 2015).

Table 1 displays a few more scientific works devoted to fertilizer nanoformulations; as it can be observed, some were synthesized to be tested on certain pests and others on crops or plants or cells. Also, they are made of different components such as polymers and although they are not listed, the synthesis methods are varied. In any case, all of them have in common that even though good results have been obtained, the toxicity issue is an important parameter to be investigated further for these nanopesticides to be potentially used in the near future.

There are studies in which the bulk formulation of a nanopesticide is assessed along with its nano-sized counterpart and it has been reported that the toxicity level is similar (Vignardi et al. 2020). However, the potential assets of nanopesticides are related to their stability, dispersion in aqueous media, and promoting a controlled release of the active compound, which, in turn, increases effectiveness (Bratovcic et al. 2021).

Being at a relatively early stage in the development of nanopesticides, it is essential that the toxicological evaluation of nanoformulations is foreseen and that it is verified that they comply with regulatory frameworks to guarantee a safe application for both the environment and human health.

While population growth and demand for food do not stop, the development of pesticidal nanoformulations and the integration of toxicity studies for their safe application make it necessary to have mechanisms for their practical implementation.

4 Nanomaterial Applications for Pesticide Detection and Removal

In agriculture, pesticides play the role of chemical agents whose task is the destruction and/or control of pests. They are of different kinds, according to the problem they attack, namely: insecticides and rodenticides (insect and animal infestation), herbicides (weeds), fungicides (fungal or mold disease), and so on (Kim et al. 2017). Despite their benefits, they are harmful at some levels to humans and the environment, particularly due to bioaccumulation and other factors. These hazardous issues come from both the use and misuse of pesticides (Caldas 2019). Still, they cannot disappear because of assets such as crop quality improvement and yield (Hassaan and El Nemr 2020).

On the other hand, nanomaterials of different types have a wide range of potential uses, ranging from electronics, to biomedicine, energy, food engineering, and construction, among others, and of course, agriculture cannot be left behind (Mandal and Ganguly, 2011; Khan et al. 2019), mostly because of their interesting and useful properties (Gatoo et al. 2014). Specifically, when it comes to pesticides,

Table 1 Research works on the development of nanofertilizer formulations

Nanoformulation type	Target pest/plant/ cells	Size (nm); concentration	Benefits	Drawbacks	References
Neem oil–corn protein nanoparticles (NPs)	*Allium cepa*, nitrogen cycle bacteria, and *Caenorhabditis elegans***	278 ± 61.5; not available (NA)	Susceptibility to the effects of neem oil, while not showing potential toxicity (*C. elegans*, *Allium cepa*)	Even though potential toxicity was not demonstrated, further studies on cell damage are recommended	Pascoli et al. (2019)
Copper based	*Porcellionides pruinosus*	–	Influence on the microbial functions related to the carbon cycle; invertebrates in soil may decrease this formulation effects to some extent	Lack of balance of the quality, fertility, and functioning of soil (effects were observed even 90 days after contamination)	Peixoto et al. (2021)
Chitosan–silicon matrix	Maize	360.5 ± 1.34 (hydrodynamic diameter); 0.01–0.16%, w/v	Enhancement of seedling vigor index; plant antioxidant defense and photosynthesis of plant; maize crop yield by seed and foliar application	Negative influence on bacterial and fungal community richness	Kumaraswamy et al. (2021)
Polymeric and lipid nanoparticles (unloaded and loaded with atrazine and parquet)	*Caenorhabditis elegans*	300–400; NA	Both nanoparticles, loaded and unloaded, present toxic effects against the tested organism	Toxicity issue needs to be improved	Jacques et al. (2017)
$Cu(OH)_2$	*Cucumis sativus* (cucumber) and *Zea mays* (corn)	50–1000; 0, 2.5, and 25 mg	Metabolic reprogramming of both plants	–	Zhao et al. (2018a)
TiO_2 nanoparticles	*Spodoptera littoralis*	125–250; 1000, 500, 250, 125, 62.5, and 31.25 ppm	The target organism was affected at certain doses of these NPs	–	Shaker et al. (2017)

(continued)

Table 1 (continued)

Nanoformulation type	Target pest/plant/cells	Size (nm); concentration	Benefits	Drawbacks	References
Eucalyptus extract-based nanocapsules	*Myzus persicae*	380 (hydrodynamic radius); 0, 10, 15, 25, 35, and 50 mg/mL	Significant mortality at 72% for 30 days	–	Khoshraftar et al. (2019)

nanomaterials can be used to produce new formulations (Zhao et al. 2018b) as already covered in the previous section but also to aid in their excess removal, mainly focused on two aspects: sensing and destroying—the first one refers to the amount detection of a certain pesticide, and the second, to the elimination of its traces (Chand Mali et al. 2020; Aragay et al. 2012).

4.1 Pesticide Detection and Removal by Means of Nanomaterials

Pesticides are one of the main causes for food contamination that, hence, also end up causing health problems. Some of the traditional techniques for their detection include high-performance liquid chromatography (HPLC), mass spectroscopy (MS), HPLC-MS/MS, and gas chromatography to mass spectrometry (GC-MS/MS), as well as electrophoresis, but it is costly because of factors such as instrumentation and the fact that a high amount of sample is required to carry out the analyses (Pérez-Fernández et al. 2020a).

Since some time ago, nanomaterials have been investigated due to the fact that they allow for contaminant detection with high sensitivity, lower cost investment, as well as the easiness for small sample preparation and use (Rawtani et al. 2018).

It has to be mentioned that nanomaterials in their different forms can be used for the detection, degradation, and removal of pesticides, thus giving a wide range of options and possibilities to remediate hazards that pesticides usually have (Worrall et al. 2018). In fact, research on nanotechnology applied to agriculture has been for 20 years around, according to the ScienceDirect and PubMed search engines; such information is depicted in Fig. 2. It can be observed that the number of published works has increased greatly from 1999.

4.2 Pesticide Detection

4.2.1 Biosensors

Biosensors are analytical devices whose purpose is the detection of a chemical substance, by combining a biological component with a physicochemical detector. In the case of pesticide detection, they are the most investigated and they are of different types (Huang et al. 2021).

Figure 3 shows the general scheme of a biosensor's functioning. First is a biological recognition element usually known as a bioreceptor, which is a molecular species that is immobilized and whose task is to permit the binding of an analyte. Then, there is the transducer element that is in charge of directly extracting the binding information resulting from the encounter with the analyte. The transducer function relies on either measuring changes in current, resistance, or charge right

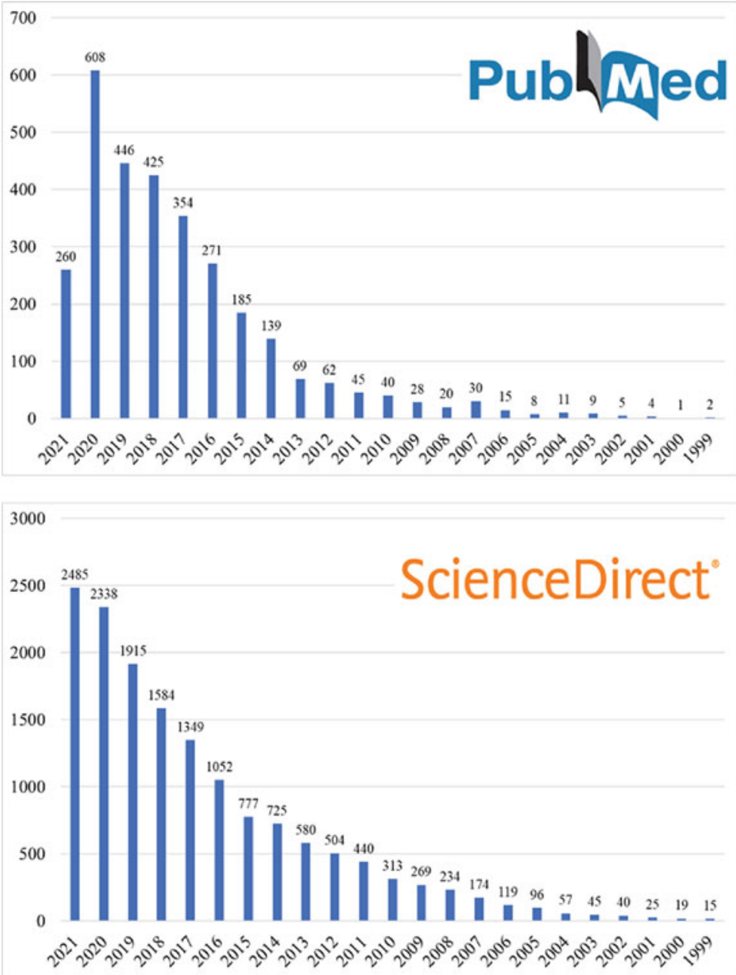


Fig. 2 Graphics show the growing tendency for scientific works published on the nanotechnology applied to agriculture topic

after a chemical reaction or the change of an optical characteristic such as fluorescence or absorbance, which is usually proportional to the analyte's concentration. Finally, the transduced signal (output) can be processed with the aid of electronics and displayed for its visualization (Bhalla et al. 2016).

Enzyme-based (enzymatic) biosensors: Their functioning is based on an enzyme acting as the recognition element in a selective manner with its substrate (analyte). They can quantify the catalysis or the inhibition of enzymes by the target analyte by two paths (Economou et al. 2017):

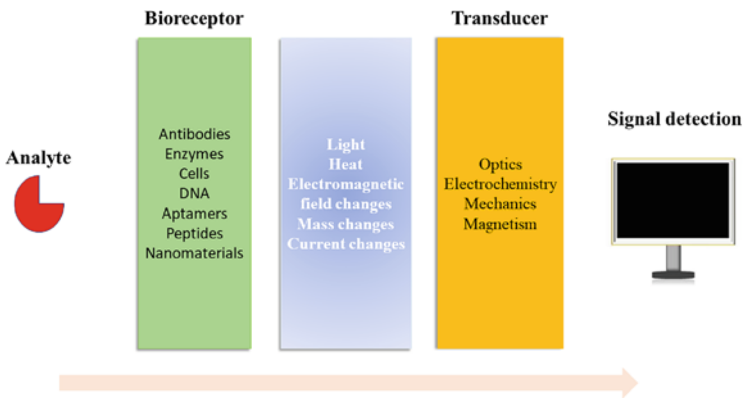


Fig. 3 Scheme of a biosensor's general functioning

(a) The enzyme able to metabolize the analyte and its concentration is found by means of the measurement of the catalytic transformation of the analyte.
(b) The enzyme can be restricted by the analyte, hence its concentration is associated with a decrease in formation of the enzymatic product.

One type or more of enzymes can be used for their development, for example: cholinesterases (ChEs) among which we can find acetylcholinesterase (AChE), organophosphorus hydrolase (OPH), and organophosphorus acid anhydrolase (OPAA). All of them are focused on the detection of different pesticides. Acetylcholinesterase biosensors are widely investigated for the detection of organophosphorus and carbamate pesticides. Organophosphorus hydrolase and organophosphorus acid anhydrolase biosensors are aimed at organophosphorus pesticide (OP) detection (Newman and Setford 2006).

Nanoarchitecture has been used in the development and design of these biosensors, for example by using nanocomposites based on metal organic frameworks, quantum dots, biodegradable polymers, magnetic nanoparticles, and so on. In fact, biosensors are the most studied structures concerning pesticides and there are different types. The subdivisions and categories may vary among different authors; hence, a general outline is given for reference:

Whole-cell biosensors: They are intended to measure functional information and the effects of an analyte on the physiological function of living cells (Bousse 1996).

Immunosensors: They are considered solid-state devices where the immunochemical reaction is coupled to a transducer. According to the type of transducer, immunosensors are subdivided into electrochemical, optical, microgravimetric, and thermometric types; some authors consider these categories apart. Their functioning is alike to the one of immunoassays: the specific recognition of antigens by antibodies to form a stable complex (Cristea et al. 2015).

DNA biosensors: These kinds of biosensors work on the principle of molecular recognition based on the alterations induced by electrochemical responses before and after a hybridization event. They are further categorized into electrochemical, optical, acoustic, and piezoelectric types (Kuralay et al. 2012; Kuralay and Erdem 2014).

Table 2 displays research works in which different examples of the aforementioned types of biosensors are listed. As it can be observed, they all detect different kinds of pesticides, work under a variety of mechanisms, and their structures are mainly based on composite materials. An important feature that is relevant is the limit of detection (LOD) that is reported to be much below the micro concentrations.

4.2.2 Other Nanostructures for Pesticide Detection and Removal

The majority of nanotechnology-based platforms aimed at pesticide detection are focused on biosensors, and they sometimes make use of nanostructures as part of them as discussed in the previous section. However, there are examples of other nanomaterials that are used, too, but they are much less covered in their research given the fact that biosensors have much more advantages due to their complex, well-organized structure and reproducibility, but a drawback they present is that they are restricted to detection only. The materials that will be covered in this section can be considered as composites due to the fact that several nanostructures act in a synergistic manner to detect, quantify, and even remove a certain pesticide; this is accomplishing a double task. When recovery rates are mentioned, it will be assumed that the mentioned composite can be reused for either detection or removal.

Colorimetric approaches have been investigated using graphene oxide nanocomposites—for instance, size-tunable graphene oxide to detect organophosphorus pesticides (OPs) at nanomolar levels by means of a cascade reaction. The mechanism basically relies on the basis of the intrinsic peroxidase-like activity of graphene oxide that leads to a color-generating reaction by means of multistep enzyme catalysis in the presence of AChE and CHO. The inhibition of AChE by OPs is observed as a decrease in color intensity, which is proportional to the concentration of OPs (Chu et al. 2020). Fe_3O_4-TiO_2/reduced graphene oxide (Fe_3O_4-TiO_2/rGO) was synthesized hydrothermally, showing an efficient peroxidase-like catalytic activity for the sensing of atrazine using TMB as a peroxidase substrate molecule with 2.98 μg/L as a limit of detection (LOD). Additionally, photocatalytic degradation of atrazine molecule at 100% under natural sunlight irradiation was attained. Interestingly, FeO4-TiO2/rGO nanocomposite was successfully recycled for ten times without a significant loss of its photocatalytic efficiency (Boruah and Das 2020).

Graphene oxide nanomaterials have been studied and even very simple but useful platforms have been synthesized: graphene nanofragments modified with chitosan (CS) and AChE were successively drip-coated onto the surface of a glassy carbon electrode using a layer-by-layer assembly approach. The target pesticide was dichlorvos and the limit of detection was 54 pM (Zhang et al. 2021).

As for noble metal nanoparticle-related methodologies, most of the research is concentrated on silver (AgNPs) and gold nanoparticles (AuNPs). There is a study in which gold nanoparticles, AuNPs, are coupled with hydrogen peroxide, which leads

Table 2 List of different pesticide biosensors

Type of biosensor	Target pesticides	Mechanism of action	Limit of detection	Reference
Whole-cell biosensor	Synthetic pyrethroid	Anti-3-PBA VHH whole-cell surfaces are the detection elements; when these cells are mixed with 3-PBA-protein conjugate, crosslinking happens and hence it can be detected	3 ng/mL	Riangrungroj et al. (2019)
Electrochemical	Paraoxon, 2,4-dichlorophenoxyacetic acid, and atrazine	Paper-based platform: the analyzed pesticides' ability to inhibit butyrylcholinesterase, alkaline phosphatase, and tyrosinase is used to establish a correlation with the pesticides' concentration by supervising the enzymatic activity in both their absence and presence	Paraoxon: 90 ± 1% and 88 ± 2%, for 10 and 20 ppb; 2,4-dichlorophenoxyacetic acid: 86 ± 4% and 93 ± 2% for 100 and 200 ppb; Atrazine: 80 ± 4% and 92 ± 3% for 50 and 100 ppb	Arduini et al. (2019)
Fiber optic	Fenitrothion	Fenitrothion interacts with a deposited silver film promoting a change in refractive index that was measurable as a red shift of 56 nm corresponding to the pesticide concentration in a range of 0.25–4 μM	38 nM	Kant (2019)
Enzyme based	Paraoxon	The Ce/UiO-66@MWCNTs@GCE complex matrix was used to load AChE onto vacant sites; the redox properties of Ce were taken advantage of also to increase electron transfer and decrease the number of diffusion pathways between the thiocholine and electrode surfaces	0.004 nM	Mahmoudi et al. (2019)

(continued)

Table 2 (continued)

Type of biosensor	Target pesticides	Mechanism of action	Limit of detection	Reference
Immunosensor	Imidacloprid	Self-obtained specific monoclonal antibodies are immobilized on the AuNP-SPCE; the measured free IMD competes with IMD conjugated with horseradish peroxidase (IMD-HRP) in order to be recognized by the antibodies; afterwards, 3,3′,5,5′-tetramethylbenzidine (TMB) is enzymatically oxidized by HRP, followed by the oxidized TMB reduction back to the surface of the SPCE; the outcome is an associated catalytic current (analytical signal) that is *inversely* proportional to the IMD concentration	22 pmol/L	Pérez-Fernández et al. (2020b)
DNA based	Profenofos	A thiol-tethered DNA capture probe, complementary to a previously selected aptamer sequence, was immobilized on gold nanoparticle/polyaniline composite film-modified electrodes (AuNP/PANI/GSPE); different profenofos solutions containing a fixed concentration of the biotinylated DNA aptamer were dropped onto the detector structures; a hybridization reaction happens and was measured using a streptavidin–alkaline phosphatase enzyme conjugate that promotes catalyzation and the hydrolysis of 1-naphthyl-phosphate; the 1-naphtol enzymatic product was detected by using differential pulse voltammetry (DPV)	0.27 μM	Selvolini et al. (2018)

to the oxidization of *o*-phenylenediamine (OPD) substrate to produce 2,3-diaminophenazine, with characteristic absorption peak at 450 nm and a yellow shade. When such system interacts with dimethoate, a pesticide, the catalytic activity of AuNPs is inhibited greatly, leading to the appearance of a light yellow hint or even colorless solutions (Hu et al. 2019). Cysteamine-modified gold nanoparticles were utilized for detecting glyphosate. Their agglomeration due to the interaction with the pesticide results in a color change from red to blue or even purple, which can be observed with the naked eye on the surface of plant tissues, but the quantification was carried out by using the generated complex (AuNPs-glyphosate) as a SERS substrate (Tu et al. 2019). In another study, dimethoate was adsorbed onto gold nanospheres and nanorods in aqueous solution using the batch technique. The best adsorption and removal results were obtained with nanospheres as monitored on a 24-hour basis (Rahmanifar and Moradi Dehaghi 2014).

Carbon-dots stabilized silver nanoparticles interacting with phoxim, aggregate, hence promoting a red shift from 400 nm to 525 nm in a linear trend, with a limit of detection of 0.04 μM and with a recovery of 87–110.0% (Zheng et al. 2018). Another similar study to detect triazophos was reported by Ma et al. (2018). Polyurethane foams were used as a substrate for silver nanoparticles coated onto polyurethane foam and glass beads in a fixed bed column, to remove chlorpyrifos in aqueous solution, by varying the flow rate (20–40 mL/h) with a fixed bed height and pesticide concentration at percentages higher than 90% (Varghese et al. 2020). Cysteine-capped Ag nanoparticles' ability to remove chlorpyrifos and malathion was assessed in a study that demonstrated that chlorpyrifos has better affinity to Ag nanoparticles compared with malathion due to the aromatic amine group present in it (Singhal and Lind 2018).

Metal oxide nanoparticles such as silver oxide (SO) ones have been loaded into chitosan to form beads for permethrin removal from water; this system works as a great adsorber with 99% of permethrin removal in 45 min shaking time, pH 7, room temperature of 25 mL solution of pesticide (0.1 mg L^{-1}). Such results were obtained by varying the mentioned parameters (Ma et al. 2018). An anatase TiO_2-carbon paste electrode was developed for the detection of cypermethrin (0.1 ppm LOD) by the accelerated electron transfer on the surface of electrode due to the compact nature of the structure and its high conductivity, which contribute to the sensing sensitivity increase with the increasing of anatase TiO_2 concentration (Nurdin et al. 2019).

Concerning carbon nanostructures, there are studies in which, for example, a carbon nanotube (CNT)/β-cyclodextrin (β-CD) nanocomposite reinforced hollow fiber (HF) was applied to direct-immersion mode of solid-phase microextraction for the determination of carbaryl and 1-naphthol in tomatoes, along with high-performance liquid chromatography. With such setup, limits of detection of 0.05 and 0.15 ng/g for 1-naphthol and carbaryl, respectively, along with the high recovery in the range of 84.2–108.9% were obtained (Ding et al. 2019). Magnetic carbon nanotubes are obtained by chemical vapor deposition (CVD); their structure is made up by hydrophobic and hydrophilic fractions that allow for the adsorption of alachlor, buprofezin, cadusafos, kresoxim methyl, disulfoton, terbufos, and trifluralin. The magnetic properties and amphiphilic character of the nanocomposite permitted the phase separation, and improved the extraction of the pesticides (Barbosa et al. 2017). It has to be pointed out that these carbon nanostructures are mainly used in the development of biosensors.

On the subject of bimetallic nanoparticles, Fe/Ni nanoparticles have been evaluated for the removal of profenofos due to their high adsorbance efficiency suggesting a spontaneous and endothermic process (Mansouriieh et al. 2016). An Au–Pd co-modified TiO_2 nanotube film was synthesized by a photo-deposition method and was later assessed for the degradation of malathion, revealing that the coupling of Au–Pd resulted in a more efficient degradation process than when they were not attached to the TiO_2 structure (Yu et al. 2010). SERS based on core-shell bimetallic Au@Ag NPs has been achieved for the detection of triazophos and parathion-methyl residues with detection limits of 0.001 mg/kg and recovery of 93.36–123.6%, respectively (Yaseen et al. 2019).

Additional nanostructured materials that can be mentioned are scheelites: these microwave-synthesized calcium tungstate ($CaWO_4$) nanoparticles were found to be good adsorbers of cyanophos, yielding dimethyl phosphorothioic acid (DMPA) as the degradation product (Yekta et al. 2016).

5 Effects of Nanotechnology-Based Pesticides on Pollinators and Nature

Even though nanotechnology is a research field with a relevant presence and with an increasing interest in its growth for potential application in several areas, the concerns related to agriculture have to do with environmental impacts, especially because although materials at the nanoscale have provided satisfactory outcomes, there is still a long way to go especially when addressing toxicity and its consequences. In the case of pesticide nanoformulations, this has to do with the effects on pollinators. There are few works related to this topic since much of the research is focused on the development of nanopesticides and, of course, evaluation of their immediate biological effects on plants, soil, and water, but an assessment of the effects on pollinators are barely carried out. The studies that can be found in literature related to nanopesticides' effects on pollinators are aimed at bees. El-Helay et al. studied the use of *Citronella* in conjunction with nicotine pesticide formulations (Nanochlorpyrifos and nanoimidacloprid) to repel bees and thus keep them safe (El-Helaly et al. 2021). Oliveira et al. studied solid lipid nanoparticles as pyrethrum carriers showing that this formulation had no significant effect on digestive cells, for honeybees (Oliveira et al. 2019). Other research on this topic is only related to regulations and possible paths to control side effects of nanopesticides (Hooven et al. 2019).

6 Conclusions and Future Perspectives

Pest management is one of the important topics when it comes to the nanotechnology–agriculture relation. The most important aspect to work upon is basically toxicity, which is an issue concerning the environment, human beings, as well as pollinators. Additionally, it is also worth considering that other types of nanomaterials have been approved for their use in commercial products whereas nanopesticides have not.

Tackling such obstacle is being worked upon by many researchers worldwide by means of the study and development of a wide variety of nanoformulations. Then, there is also the part related to the remediation of their adverse effects by using nanobiosensors. This implies that there is an opportunity to use them synergistically to enhance crop production in the long run.

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Nanotechnology in Water and Wastewater Treatment

Siba Soren, Pravati Panda, and Subhendu Chakroborty

1 Introduction

About 75% of the earth contains water in different forms. Human civilization is nothing without water. With human civilization's growth, water consumption has been increased in many different ways, like industrialization and urbanization. Clearly, there is contamination of earth's drinking water with heavy metal ions, fluoride, organic dyes, biomolecules, etc., which has built into a global environmental issue. The displacement of heavy metal ions like $Cr^{3+/6+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Ag^{1+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} to water bodies has led to their accumulation in the food chain, leading to a threat to human's health (Godwill et al. 2019; Arif et al. 2015; Jessica et al. 2020; Eline et al. 2019). Though nature has remedies for this problem through the aquatic animals, the cycle again comes to human health in the food chain due to consumption of aquatic animals. Here it is necessary to discuss the adverse effects of water pollutants, which can be termed as carcinogens or toxic materials (Afroze and Sen 2018; Cocarta et al. 2016). According to the findings of researchers, Cr(VI) ions are the most carcinogenic of the Cr(III) group of water contaminants (Marina et al. 2020). The impaired cognitive developments like increased hyperactive behavior and low IQ level are significant results of Mn's excess level in drinking water (Khan et al. 2012; Leonhard et al. 2019; Bouchard et al. 2011). Chronic iron toxicity and neurological and cardiovascular disorders are directly related to overload of Fe and Co ions (Siri-Angkul et al. 2018;

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Unice et al. 2014). Excess Ni can induce toxicity in various metabolic active tissues (Kusal et al. 2019). Even essential elements, like copper and zinc, cause serious health effects like low blood pressure, vomiting, and nausea, when taken in excess in oral drinking water. Except for the first row of the transition metal ions, elements like Cd^{2+}, Hg^{+2}, and Pb^{+2} come under the most toxic elements causing long-term liver and kidney damage, renal dysfunction, serious blood disease, and neurotoxicity (Keshavarz et al. 2013; Chen et al. 2011; Rafati et al. 2017; Krishna and Sunil 2018). Hence, modern techniques are being used to separate heavy metal ions from water. Membrane filtration, adsorption, chemical precipitation, ion exchange, electrochemical treatment (Lopez et al. 2019; James et al. 2019; Davarnejad and Panahi 2016; Khulbe and Matsuura 2018; Tran et al. 2017), etc. have been developed over the traditional technique to purify contaminated water within a short time period. Also, combining different techniques for better wastewater treatment is under consideration (Huang et al. 2016; Raffaele et al. 2020).

Besides the heavy metal ions, pharmaceuticals and textiles effluents (dyes) constitute 1–20% of the wastewater component worldwide, which influences ecosystem and eutrophication and thus human health (Saravanan et al. 2013; Chen et al. 2017; Ezechi et al. 2015). Effluents are classified based on color, functional group present, and ionic charge (cationic–basic and anionic–acidic, reactive, direct) formation upon dissolution in water present (Clarke and Anliker 1980). At the same time, vats and dispersed dyes are nonionic charges (Tan et al. 2015). Lastly, halogen group fluoride is the most reactive element that attacks oxygen and changes the metabolism, leading to hydrogen peroxide production. Simultaneously, excess fluorine takes part in free radical formation (Yang and Liang 2011). According to the World Health Organization, the recommended amount of fluorine is 1.5 mg/L^{-1}. But drinking water or groundwater has exceeded the amount of fluorine from geogenic and anthropogenic sources. It is expensive and difficult to remove excess fluoride from water. Hence, physiochemical technique based on adsorption method is widely used for removal of fluorine.

With human society's development, groundwater and water sources have become polluted with various pollutants and cannot be used for drinking. In recent decades, lots of nanomaterial technologies have been applied to wastewater treatment for supply of clean water, using removing, adsorbing, and filtration methods.

2 Nanotechnology for Wastewater Treatment

The twenty-first century is running through nanotechnology. This technology has spread over all the industries, from problem-solving to making new things. The development of various tools and techniques enabled by nanotechnology opens up a new potential alternative to treat wastewater more efficiently and cost-effectively (Baruah et al. 2012; Sunandan et al. 2016). Nanomaterials are the main ingredients of nanotechnology in the detection and removal of various water pollutants. This is because nanomaterials are of small dimensions, have well-organized structure at atomic and molecular levels, are highly reactive, more accurate, and, most importantly, they can be produced by environment-friendly techniques that are potentially cost-effective (Fernanda et al. 2018; Hornyak et al. 2009). Some of the promising water treatment techniques introduced by nanotechnology are discussed below.

2.1 Nanophotocatalysis

Typically, inorganic metallic/metal oxides and semiconducting materials within the range of 1–100 nm are used in photocatalysis. They are readily available, inexpensive, and less hazardous, in addition to being chemically stable and having good photoactive characteristics (Ciambelli et al. 2019). These metallic/metal oxide nanoparticles (NPs) show photocatalytic activities only when they interact with light energy and mineralize/degrade organic substances (including pharmaceutical compounds) and microorganisms (bacteria) via the reaction with hydroxyl radicals (Chen et al. 2018; Sarkar et al. 2015; Tahir et al. 2019) through "heterogeneous photocatalysis" process. Among all the common metal oxide nanophotocatalysts such as TiO_2, ZnO, SiO_2, and Al_2O_3, TiO_2 is an excellent natural photocatalyst material (Sherman 2003; Ali et al. 2019; Bhanvase et al. 2017; Min et al. 2015) (Fig. 1).

2.2 Nanofiltration

An alternative promising thin polymeric membrane having <0.001 μm pore sizes is used as a nanofiltration (NF) over conventional filtration method with rejection ability between reverse osmosis (RO) and ultrafiltration (Cheng et al. 2015; Wu et al. 2014; Li et al. 2014; Galanakis et al. 2012; Donnan 1995; Bowen and Welfoot 2002; Oatley et al. 2012; Hilal et al. 2005). Nanofiltration membrane easily captures

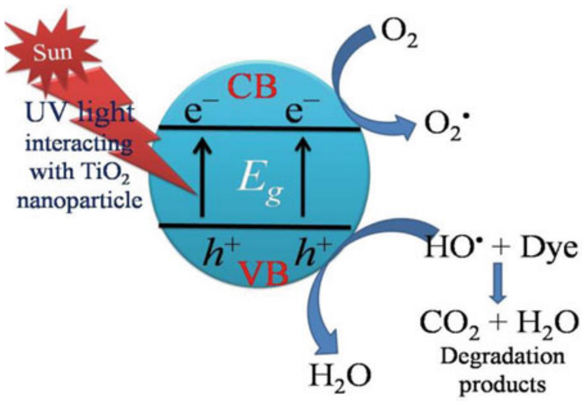

Fig. 1 TiO_2 photocatalytic mechanism on dye degradation under solar light irradiation process

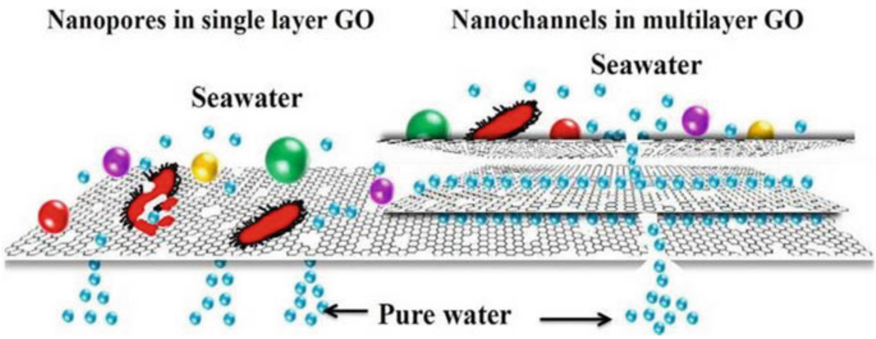

Fig. 2 Nanochannels in graphene oxide (GO) membrane pore for water flow. (Reproduced from (Ananda et al. 2018), with permission from Elsevier)

multivalent ions that are difficult to pass through membrane while monovalent ions and solvent molecules can easily move through nanofiltration membrane. The salt rejections of nanofiltration depend on the membrane surface and pore size, interaction of ions/hydration at the nanopores, and size of the ions. The modification in the membrane charges also results in the exchange of weak ions through nanofiltration (Mikulasek and Cuhorka 2016). NF has more positive rejection capabilities toward divalent ions than monovalent ions. Besides these, NF can act in low operating pressures and high water fluxes (Du et al. 2016; Park et al. 2016). Typically, 50–90% of monovalent ions such as sodium or chlorides can be removed by nanofiltration membranes. Scientists are working on NF membranes for better efficiency in the removal of monovalent anions and salts (Perez-Gonzalez et al. 2015). Ananda et al. studied carbon-based nanoporous membranes with desired spacing between layers to reveal the promising materials for future nanofiltration technology capable of rejecting monovalent ions (Ananda et al. 2018). Moreover, some heavy metals like Mn^{2+}, Cu^{2+}, As^{3+}, As^{5+}, Cd^{2+}, and Pb^{2+} can be filtered from water solution using absorption and nanofiltration membrane (Al-Rashdi et al. 2011) (Fig. 2).

2.3 Nano Adsorbents

Adsorption methods are considered very appropriate methods among all the above techniques. In these techniques, cheap adsorbents with high-efficiency materials are being used, which are versatile and easy to control without any pre-treatment step (Wang et al. 2005; Yadanaparthi et al. 2009). The nature of adsorption can be physical, chemical, or exchange adsorption (Wong et al. 1997). Nanomaterials are considered effective and potential adsorbents due to low-temperature modification and different surface chemistry compared to bulk materials (Khin et al. 2012). The properties of high affinity to adsorb waste or unwanted elements by nanomaterials are based on its diverse morphologies. There is a balance between the energy developed from elastic deformation, polar charges, and nanomaterials' surface areas. These nano adsorbents' physicochemical characteristics led to its increasing application as a sorbent for wastewater treatment (El-Sayed 2019).

3 Metal/Metal Oxide Nanoparticles for Purifying the Water from Organic and Inorganic Waste

Wastewater treatment by conventional methods is of poor treatment efficiency and can be limited. Therefore, nanotechnology approaches are a proper method to wastewater treatment with nanomaterials by using various properties like adsorption, degradation, and filtration of impurities present in water bodies.

3.1 TiO_2 Nanoparticles as Photocatalyst and Adsorbent

Titanium dioxide can easily be reduced to tiny structures, shapes, and sizes (Banerjee 2011). Photoexcitation of semiconductors depends on the bandgap energy. The TiO_2 semiconductors have existed in rutile of 3.0 eV bandgap and anatase phase having 3.2 eV. Photoexcitation of anatase lies in the ultraviolet (UV) range at 388 nm wavelength whereas rutile absorbs visible light at 410 nm wavelength. Various factors affect the efficiency of photocatalyst like the intensity of light source (Karunakaran and Senthilvelan 2005), nature of photocatalyst (Kogo et al. 1980; Ding et al. 2005; Gao and Liu 2005), pH of solutions (Haque and Muneer 2007), temperature, and the quantity of photocatalyst (Krýsa et al. 2004; Chun et al. 2000). In terms of thermodynamic and kinetical stability, most research papers show the contradiction point on the rutile and anatase phase of TiO_2 (Suresh et al. 1998; Zhu et al. 2005; Zhang and Banfield 2000; Gouma 2003). In contrast, the metastable brookite phase is reported as difficult to synthesize (Beltran et al. 2006). Fox and their co-researchers studied the photocatalytic behavior of all kinds of titanium dioxide phases. They have claimed that commercial TiO_2, Degussa P25 (25% rutile and 75% anatase), has higher photocatalytic activity than 100% anatase (Fox and Dulay 1993). The improvement in the degradation process was observed by commercial TiO_2 when it was annealed in vacuum and air at various temperatures. The results show photocatalytic activity toward fenarimol degradation was significantly increased by annealing in a vacuum. The photocatalyst degradation's better efficiency after annealing can be explained by generates of Ti^{3+} sites or oxygen vacancies that prevent the electron-hole recombination (Bessergenev et al. 2015). The most reactive azo dye, reactive orange 4 (RO4), was decolorized and degraded by Muruganandham et al. using TiO_2 (anatase) and TiO_2-P25 (Degussa) using advanced oxidation processes (AOPs). The order of reactivity of photocatalysts is TiO_2-P25 > TiO_2 (anatase) (Muruganandham and Swaminathan 2004).

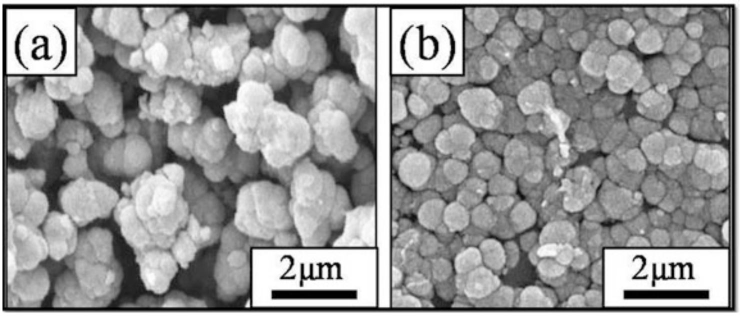

Fig. 3 SEM images of (**a**) pure TiO_2 anatase nanoparticles and (**b**) after adsorption of mercury(II). (Reproduced from (Ghasemi et al. 2012), with permission from Elsevier)

On the other hand, heavy metal ions are separated through the bulk and nanoparticles of TiO_2. The anatase phase's different surface planes can regulate the catalytic reactivity, chemical behavior, and surface acidity (Martra 2000). Specific surface areas play a crucial role in anatase TiO_2 nanoparticles. Engates et al. reported that metal (Zn, Cd, Pb, Ni, Cu) adsorption capacity of nano-sized TiO_2 (8.3 nm) is more than bulk because of maximum specific surface area, 185.5 m^2/g, compared to bulk (329.8 nm), 9.5 m^2/g. Their test was carried out with Antonio tap water and a solution of pH 8. Results have shown that nano-TiO_2 had faster adsorption than the bulk-TiO_2, followed by a modified first-order model that supports Langmuir isotherm on metal adsorption by TiO_2 anatase (Engates and Shipley 2011). Besides the above metal ions, a very high toxic and hazardous element like mercury(II) ion has been successfully adsorbed from aqueous solution by mix phase (i.e., 13.2% anatase and 86.8% rutile) of TiO_2 nanoparticles with surface area of 98.743 m^2/g. Its scanning electron microscopy (SEM) results are shown in Fig. 3. The smooth surface in Fig. 3b reveals Hg(II) ions are adsorbed on TiO_2 nanoparticles after the adsorption process (Ghasemi et al. 2012). Hence, commercial as well as laboratory-synthesized TiO_2 nanoparticles are considered better adsorbent.

3.2 *CeO_2 Nanoparticles as Photocatalyst and Adsorbent*

Among rare earth oxides, cerium oxide is taken as a useful, common metal oxide for industrial applications (Yabe and Sato 2003; Wang et al. 2007; Brosha et al. 2002) by tuning its oxidation state between +3 and +4 and vice-versa. Its adsorptive properties significantly change with surface area, size, shape, and morphologies. CeO_2 nanoparticles were synthesized under alkaline (Zhang et al. 2004; Mishra et al. 2018) and neutral conditions (Soren et al. 2015). In alkaline medium, CeO_2 nanocrystals were stabilized by hexamethylenetetramine (HMT) to prevent agglomeration leading to the formation of 12 nm nanocrystals, while 8 nm CeO_2 nanocrystals were synthesized under neutral conditions using the 1,4-butanediol, which acts as reducing agent. The spherical agglomerated ceria nanoparticles of specific surface area (47.73 m^2/g) were used for overall decolorization of both the dyes alizarin red S (ARS) and eriochrome black T (EBT) under visible light irradiation (Mishra et al. 2018). Besides this, the hollow interior space of 14-nm-sized CeO_2 nanospheres showed 70 times higher adsorption for Cr(VI) and Pb (II) heavy metal ions (Chang-Yan et al. 2010) than commercial bulk ceria material. Along with spherical shapes, other morphological structures are also reported for wastewater treatment (Liu et al. 2009; Yu et al. 2005; Si et al. 2005; Zhong et al. 2007; Strandwitz and Stucky 2009).

4 Carbon Nanomaterials

Carbon materials like charcoal, carbon nanotubes (CNT), graphene oxide (GO), and fullerenes are available for chemical reactions and adsorption. Generally, these carbonaceous nanomaterials are of hydrophobic nature, H-bonding, and π–π stacking, which helps remove dyes through electrostatic and covalent interactions. Among the various allotropic forms of carbon, the one-dimensional (1-D) CNT is an attractive nanomaterial. Next, at a higher dimension, graphene oxide (GO) is a two-dimensional (2-D) macromolecule having functional group environment (epoxy, hydroxyl, and carboxyl groups) (Dreyer et al. 2010). The positively charged molecules are strongly attracted toward oxygen atoms because of strong electrostatic interactions (Xu et al. 2009; Machida et al. 2006; Cho et al. 2010; Seredych and Bandosz 2008; Matsuo et al. 1999; Liu et al. 2002). Both skeletons are under graphene structure. However, there are significant differences in the oxygen content. The oxygen content of GO is higher than CNTs (commonly lower than 5 wt.%) (Sun et al. 2002).

In this chapter, we have shown the capacity to remove waste or unwanted gradients from water using 1-D carbon.

4.1 One-Dimensional Carbon Nanotube (1-DCNT)

In the last two decades, carbon nanotubes (single-walled and multiwalled) have been the most appropriate materials to solve the problem of environmental pollution. Highly porous and hollow structure CNT bundles have four possible sites (Ren et al. 2011), (1) internal sites, (2) interstitial channels (ICs), (3) grooves, and (4) outside surface, which contribute to the removal of organic chemicals (Goering et al. 2008; Hyung and Kim 2008) and heavy metal ions (Li et al. 2002, 2003a; Chen and Wang 2006) from aqueous solutions (Fig. 4).

The removal of highly toxic Cr(VI) was studied using CNTs as adsorbent under extreme conditions (Guoqiang et al. 2018). Generally, pristine CNTs are of lesser choice than functionalized CNT because of impurities. Also, the vital properties of CNT can be altered due to presence of surface impurities. Due to these reasons,

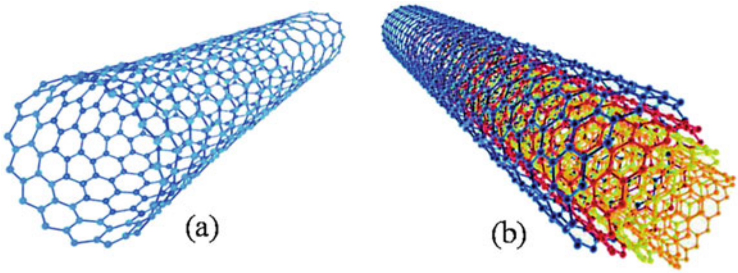

Fig. 4 (**a**) Single-walled carbon nanotube. (**b**) Multiwalled carbon nanotube (Reproduced from (Norizan et al. 2020), with permission from RSC)

CNTs are treated with acidic solution and/or in some cases in alkaline solution to remove impurities. In other cases, the functionalization process on the CNTs' surfaces can alter the surface properties and increase the solvents (Georgakilas et al. 2002) by strong electrostatic forces and replace the weak van der Waals forces (Hu et al. 2009). The comparative research on heavy metal ions' removal with pristine and functionalized CNTs reveals that functionalized CNTs exhibit the best removal adsorbent. About 0.2 g of functionalized CNTs adsorb 94.5% of Cu^{2+} ion in pH 5 at 90 °C within 94.5 min, while keeping the same condition pristine CNT removes only 61% (Mubarak et al. 2012). The adsorption of metal ions like Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} has been studied by Rao group with raw CNT and modified CNT surfaces by oxidation process (Rao et al. 2007). Their result also showed the best adsorptive properties with surface-functionalized CNTs by HNO_3, NaOCl, and $KMnO_4$. It may be concluded that the functional groups (carbonyl, hydroxyl, and carboxyl) present on the surface of CNTs are the leading groups for better ionic interaction with those metal ions after the CNTs' surface functionalization process. Except for heavy metal ions' removal, fluorides were successfully removed from water by Li et al. using aligned carbon nanotubes (ACNTs). Their results reveal its higher adsorption efficiency than soil, γ-Al_2O_3, and activated carbon in a broad range of pH (3, 5, 7, 9, and 11) at 25 °C. The active sites present on the surface and inner cavities, and the inter-nanotube connection make the ACNT superior sorbents for fluoride (Li et al. 2003b) (Fig. 5).

Simultaneously, multi-walled carbon nanotube (MWCNT) easily separates organic cationic dyes (methylene blue (MB) and acid red 183) from wastewater through electronic and π–π interactions. The surface adsorption of small MB molecule on MWCNT is due to hydrophobic and π–π interactions (Fig. 6a), while larger molecule AR183 is itself vertically oriented against the CNT wall (Fig. 6b), when they are taken in single adsorption studies. On the other hand, MB molecule is generally adsorbed on the surface of CNT because of the π–π bond at the time of dye adsorption in a binary system (Fig. 6c). There is a competition between two dyes; when they are taken as fixed amount, one of them, with higher concentration, is being adsorbed on adsorbent CNT in a binary system (Wang et al. 2012).

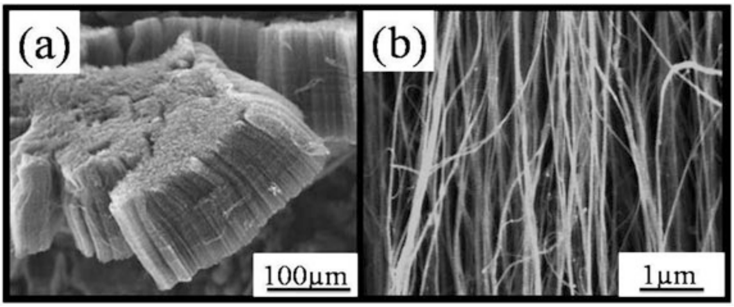

Fig. 5 SEM images with (**a**) low magnification and (**b**) high magnification of aligned carbon nanotube (ACNT). (Reproduced from (Li et al. 2003b), with permission from Elsevier)

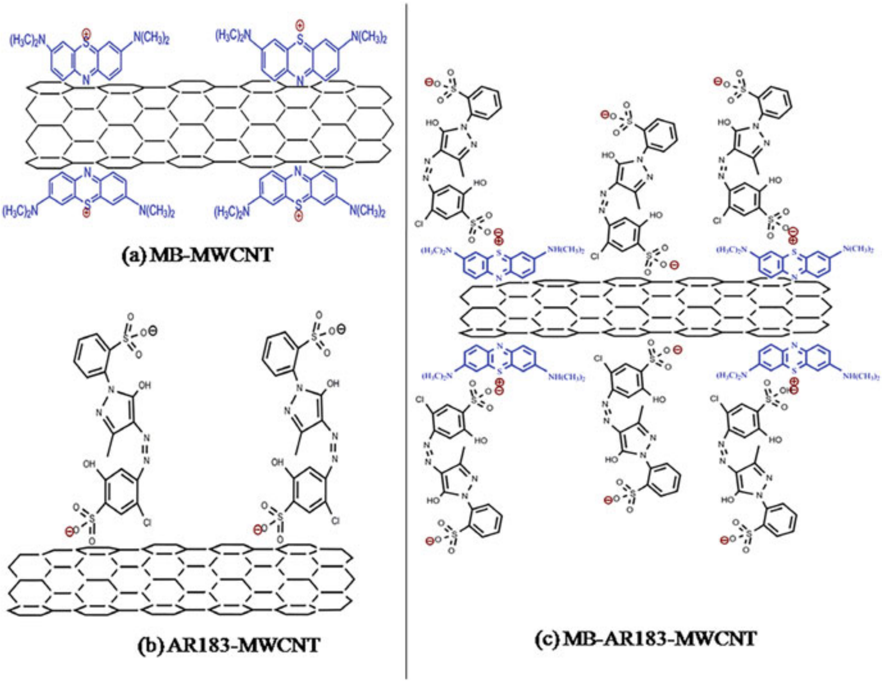

Fig. 6 Dye adsorption on MWCNT in single- and binary-dye solutions. (Reproduced from (Wang et al. 2012), with permission from Elsevier)

5 Chitosan

The second most abundant natural polymer, chitosan, with macromolecular structure, nontoxicity, cationic nature, biocompatibility, biodegradability, antibacterial activity, more active sites, and high adsorption capability, is the first choice of

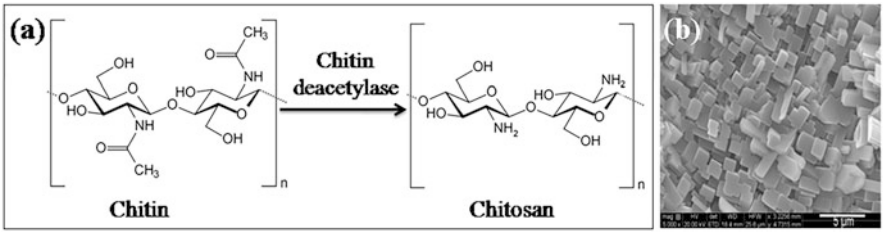

Fig. 7 (**a**) Chitosan polymer and (**b**) scanning electron microscopy of 100-nm-sized chitosan. (Reproduced from (Sivakami et al. 2013), with permission from Elsevier)

polymer for adsorbing different pollutants from aqueous solution (Nie et al. 2014). The partially deacetylated cellulosic derivative biopolymer obtained by the alkaline deacetylation of chitin is renewable and more economically attractive than other synthetic polymers. This linear polymer structure has glucosamine and acetyl glucosamine (poly-β-(1→4)-2-amino-2-deoxy-*d*-glucose) units with NH_2 and OH groups (Fig. 7a) responsible for adsorbing heavy metals from wastewater (Renault et al. 2009). Though chitosan is a promising adsorbent, it has limitations in its solubility, which is possible only in acidic pH (below pH 5) (Szyguła et al. 2009; Rinaudo 2006; Andres et al. 2007). To overcome these limitations, Sivakami et al. modified chitosan macromolecules to nano sizes (Sivakami et al. 2013), as shown in Fig. 7b.

Except for macrostructure, nano chitosan shows good performance in heavy metal ion adsorption (Qi and Xu 2004). Chitosan has high selective chelation power toward transition metals and group III ions at low concentrations (Rorrer et al. 1993), and at the same time, there is a lack of interaction toward group I and II metal ions (Muzzarelli 1973, 1977). Masri et al. reported that chitosan amino groups have higher chelation power in comparison to any other biopolymer (Masri et al. 1974). In contrast with chitosan, different scales found from porgy, flounder, and cod type fish were tested for removal of metals ion (Cu^{2+}, Zn^{2+}, Cr^{3+}, Cd^{2+}, and Pb^{2+}), as experimented by Yang and Zall (Yang and Zall 1984). They figure out that chitosan is better and relatively faster than the other adsorbents in adsorption of metal ions through internal chitosan particles. Other studies have been done with chemically synthesized highly porous chitosan with surface area 156 and 94 m^2/g for removal of cadmium ions from aqueous solution. The adsorption behavior of porous structure had a significant effect on adsorption capacity (Rorrer et al. 1993). Various interactions (intermolecular, electrostatic) are established between organic dye molecules and excellent chitosan polymer. Several workers show the potential removal of azo dyes like Congo-Red, Alizarin-Yellow, and Orange-I with chitosan by intermolecular interactions (Yamamoto 1984). Also, electrostatic interactions between chrome violet and chitosan were studied by Shimizu et al. (Shimizu et al. 1995). On the other hand, functionalized chitosan modified with salicylaldehyde, β-cyclodextrin, and a crosslinked β-cyclodextrin polymer were studied as adsorbents of phenol, *p*-chlorophenol, and *p*-nitrophenol from aqueous solutions (Li et al.

2009). The higher phenolic adsorptions were shown by β-cyclodextrin and crosslinked β-cyclodextrin due to hydrophobic and hydrogen bond interactions with phenol groups of organic species, whereas π–π interaction occurs between phenol and aromatic rings of salicylaldehyde. In the case of *p*-nitrophenol, adsorption by all modified salicylaldehyde has higher capacity maybe due to the nitrogen in -NO_2 group, while the aldehyde *p*-chlorophenol sorption by β-cyclodextrin and phenol by crosslinked β-cyclodextrin occur from pH 9.0 onward. Finally, we can conclude that the biopolymer chitosan, in all kinds and forms (macro, nano, porous, and functionalized), can be used for wastewater treatment.

6 Future Perspective of Nanotechnology in Wastewater Treatment

Nanotechnologies with nanomaterials have advantages over conventional techniques for wastewater treatment. Still, there is a need for novel advanced water technology. The need for advanced technology is due to following point of views:

1. NPs can get accumulated over a longer period of time when they are released to the environment for wastewater treatment.
2. In the synthesis of NPs, somehow hazardous chemicals and materials are being used to produce toxic reagents, and harmful solvents are merged with water sources as a by-product. Hence, NPs' preparation should be cost-effective with green synthesized approaches.
3. The most crucial factors, such as the concentration of hydrogen ions in water (pH), affect the technique's efficiency from laboratory to field experiment. It might have significant effects on natural water's physicochemical characteristics and might necessitate an additional treatment step.

Thus, using these points, nanotechnology in the laboratory investigations can have desired outcomes in improving wastewater treatment and producing quality water, which will benefit human health and well-being.

7 Conclusion

Nowadays, nanotechnology offers a very good route to wastewater treatment free from environmental pollution. Metal/metal-based oxide, a vast variety of carbon-based nanomaterials, and chitosan-modified nanomaterials seem to be the most promising candidates to remove heavy metal adsorption and dye degradation in laboratory research. But we cannot neglect their risks and impacts when we develop them. Although nanocatalysts and nanomaterials are synthesized via green methods, significantly encouraging the removal of aqueous pollutants, further research is needed for the beneficial use of such NPs and their potential toxicity toward the environment and human health.

This chapter provides an overview of the influence of water pollutants on human health and nanotechnology on wastewater treatment, which will help understand the separation/purification mechanism for future development in nanotechnology.

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Conflict of Interest The authors declare that they do not have any conflict of interest.

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Application of Nanotechnology in Plant Growth and Diseases Management: Tool for Sustainable Agriculture

Asha Humbal and Bhawana Pathak

1 Introduction

Presently, all around the globe agriculture system is facing many challenges including climate change, urbanization, sustainable use of resources, and environmental issues such as runoff, or excess use of chemical fertilizer and pesticides. These situations are further worsened by an alarming increase in food demand as the graph of the population is continuously increasing (Chen and Yada 2011). Specifically, developing countries suffer from greater challenges because the main part of their national economy depends on the agricultural sectors. Furthermore, developing countries also face some critical issues such as poverty, malnutrition, reduction of agricultural land, and lack of new arable soil (Prasad et al. 2017). Approximately one-third of world's crop yield is expected to be lost annually. The loss is attributed to different pressures, such as an infestation of rodents, natural calamities, soil infertility, microbial diseases, and weeds (Baker et al. 2017). In addition, as per the FAO (2017), by 2050, the global population will reach 10 billion, while food demand will increase by 50%, specifically in developing countries. Furthermore, there are around 815 million people who are undernourished at present and an additional 2 billion individuals are expected to be in this category by 2050. This scenario requires profound changes in the system of global food production (Usman et al. 2020). In this technological era, nanotechnology is a forthcoming technology that can help in the reform of the modern agriculture system and add tremendous value to current food security. Specific applications such as nanofertilizers and nanopesticides for trial products and nutrient levels are important interests in the

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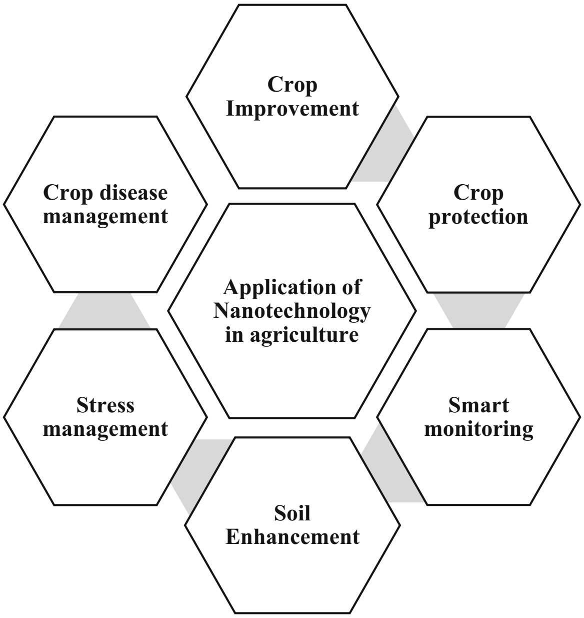
Fig. 1 Different applications of nanotechnology in agriculture



use of nanotechnology in agriculture in order to improve yield without decontaminating soil and water and also to protect against a variety of pests (Prasad et al. 2017). Nanotechnology can be able to replace the huge quantity of agrochemicals by employing various nanoparticles (NPs) for the production of crops and control of pests (Singh et al. 2020). In addition, nanoscale devices are capable to diagnose and treat an infection long before the symptoms at the macro-scale become apparent (Srilatha 2011). Nanotechnology in agriculture will help to develop agriculture as well as food industry through revolutionary new technologies like precise farming, increased nutrient absorption capacity of plants, more effective and targeted delivery system, disease identification, and disease control. Use of nanotechnology in agriculture system is expected to become powerful economic strength in the coming years (Shang et al. 2019). There are numerous applications of nanotechnology, which can be applied for sustainable agriculture as shown in Fig. 1.

2 Synthesis of Nanoparticles

Synthesis of nanomaterial or nanostructures is considered as the key component for nanoscience and nanotechnology. Nanostructured materials of appropriate size, form, shape, chemical composition, and crystalline structure only are applicable for use. Two different basic approaches of synthesis are used to produce nanomaterial of appropriate sizes, shapes, and functionalities as shown in Fig. 2. One is the top-down approach and another is the bottom-up approach. A top-down

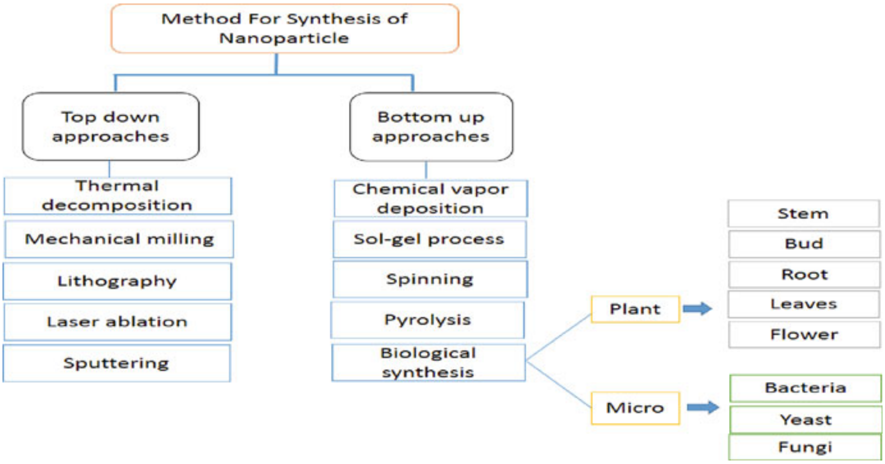


Fig. 2 Approaches for the synthesis of nanoparticles

approach is mainly based on the breaking down of bulk material into the small-sized nanostructure material. Breaking down of material in the top-down approach is mainly done through physically breaking down the bulk material to make a smaller molecule. Milling, sputtering, laser ablation, spark ablation, and grinding are a few of the lithographic methods that can be applied to produce fine particles (Rai et al. 2016). Top-down approaches are found to be more, easy, fast, and mainly dependent on the bulk material removal or separation, or bulk fabrication process miniaturization, to achieve the desired suitable properties. The bottom-up approach is simply defined as the building of the material from its bottom. The bottom-up approach includes the manufacturing of nanoparticles through the self-assembly of atoms (Thakkar et al. 2010). The bottom-up approach mainly uses chemical and biological methods. The bottom-up approach has the potential to generate less waste, therefore it is considered as more economical.

Based on the method used for the synthesis of nanoparticles, it can be divided mainly into three classes: (1) physical method, (2) chemical method, and (3) biosynthesis.

2.1 Physical Method

Synthesis of nanoparticles by physical method involves mechanical milling (MM), laser ablation, lithography, thermal decomposition, and sputtering. A suitable power charge (typically an elemental blend) is placed in high-energy mill, along with a suitable milling medium, into mechanical milling (MM). The aim of milling is to reduce the particle size and transform particles into new phases. For the synthesis of nanomaterial, various types of ball milling can be used, in which balls impact the power charge (Yadav et al. 2012). For making the colloidal nanoparticles in a different solvent, laser ablation techniques are commonly used. The pulse laser ablation technique takes place in a vacuum-sealed chamber that contains inert gases. The laser ablation method does not use any chemicals for the development of colloidal NPs, which is a major advantage of this method over the other methods used to make colloidal particles (Iravani et al. 2014). Thermal decomposition method is mainly used for the synthesis of the monodispersed nanoparticle product (Odularu 2018).

2.2 *Chemical Method*

Synthesis of nanoparticles via chemical method includes chemical vapor decomposition, sol–gel method, sonochemical method, coprecipitation, and pyrolysis and spinning technique. The chemical vapor deposition method is mainly used to make two-dimensional (2D) nanomaterials and thin film on a solid surface. In this method, chemical reactions occur between the precursors and substrate at high temperature and vacuum in the chamber (Behera et al. 2020). The sol–gel method is generally used to prepare materials such as silica, ceramic, and glass, due to its potential to make pure and homogenous materials in mild conditions. The mechanism of the process comprises hydrolysis and condensation of metal alkoxides or inorganic salts in the presence of a mineral acid (Rahman and Padavettan 2012). Coprecipitation method is used for the synthesis of magnetic nanoparticles such as Fe oxide nanoparticles. In this process, precipitation of Fe^{2+} and Fe^{3+} salt (e.g., nitrate, chloride, and sulfate) solution occurs by the addition of base. Comparatively, physical and chemical methods are considered as rapid, as they require less time, and easier methods than the biological method for the nanoparticle synthesis. However, these methods involve the excess use of toxic and harmful chemicals, require high energy and high cost, and it also affects the environment when these harsh chemicals dispose into the environment.

2.3 *Biosynthesis of Nanoparticles*

Biosynthesis involves the biological entities for the synthesis of nanoparticles such as using microorganisms (bacteria, algae, fungi, yeast, etc.) or plant parts (leaves, stem, root, bud, flower, etc.). Biosynthesis of nanoparticles is considered an eco-friendly method for nanoparticle synthesis as this method does not involve any toxic or harsh chemicals. Moreover, it is cost-effective, more biocompatible, having more stability, and this method uses universal solvent water (Li et al. 2007). In case of nanoparticle synthesis from different plant parts or plant extract, it is found that plant metabolites such as organic acid, protein, vitamins, terpenoids, flavonoids, alkaloids, and polyphenols are responsible for the nanoparticle synthesis (Devatha and Thalla 2018). Microorganisms are also used for nanoparticle synthesis as they contain reductase enzymes, prions, metal resistance genes, and organic materials that play an important role in reduction of the metal salt into the nanoparticles (Lee et al. 2020).

2.3.1 Plant Extract

Numerous researches have been published, in which different plant parts and extract including stem, root, flower, and fruit could were used for the nanoparticle synthesis. Wide range of biomolecules like co-enzymes, proteins, and secondary metabolites are present in the plant, which helps in the synthesis of nanoparticles (Venkateswarlu et al. 2013). Many studies are reported on the use of different plants or plant parts for nanoparticle synthesis, as shown in Table 1.

2.3.2 Microorganism

Wide range of bacteria could be used for the synthesis of nanomaterial. Besides bacterial species, fungus and yeast are also used for nanomaterial synthesis. The fungi contain the intracellular enzyme that acts as the reducing as well as capping agent for nanoparticle synthesis (Lu et al. 2006). Yeast is unicellular microorganism having more than 1500 species reported. Many scientists reported that yeast could be used for the synthesis of nanoparticles. Syntheses of different nanoparticles via microorganisms are shown in Table 2.

Table 1 Synthesis of nanoparticles (NPs) using different plants\plant parts

Type of NPs	Plant used	Plant part used	Size of synthesized NPs	Reference
Cu	*Ixora coccinea*	Leaf	80–110 nm	Yugandhar et al. (2018)
Au	*Syzygium aromaticum* (clove buds	Bud	5–10 nm	Raghunandan et al. (2010)
Au and Ag	*Aloe barbadensis Miller*	Leaf	10–30 nm	Chandran et al. (2006)
Cu	*Tinospora cordifolia*	Leaf	50–130 nm	Sharma et al. (2018)
ZnO	*Albizia lebbeck*	Stem	66.25 nm	Umar et al. (2019)
ZnO	*Trifolium pratense*	Flower	100–190 nm	Dobrucka and Długaszewska (2016)
ZnO	*Azadirachta indica*	Leaf	40 nm	Elumalai and Velmurugan (2015)
Cu	*Magnolia kobus*	Leaf	40–100 nm	Lee et al. (2013)
Cu	*Morus alba L.*	Fruit	50–200 nm	Razavi et al. (2020)

Table 2 Synthesis of nanoparticles (NPs) using different microorganisms

Type of NPs	Name of bacteria/fungi/yeast	Size of NPs	References
Ag and Au	*Streptomyces* sp.	Ag 8.4 nm; Au 10 nm	Skladanowski et al. (2017)
CuO	*Streptomyces* sp.	70–80 nm	Hassan et al. (2019)
Ag	*Rhodococcus* sp.	5–50 nm	Otari et al. (2015)
Au	*Nocardiopsis* sp.	11.57 nm	Manivasagan et al. (2015)
Ag/AgCl	*Macrophomina phaseolina*	5–30 nm	Spagnoletti et al. (2019)
Fe_2O_3	*Alternaria alternata*	75–650 nm	Sarkar et al. (2017)
Pd	*Saccharomyces cerevisiae*	32 nm	Sriramulu and Sumathi (2018)
Au	*Magnusiomyces ingens LH-F1*	20–28 nm	Qu et al. (2018)
Pd	*Chlorella vulgaris*	70 nm	Mishra et al. (2020)
ZnO	*Pichia kudriavzevii*	10–16 nm	Moghaddam et al. (2017)
CdTe	*Saccharomyces cerevisiae*	2–3.6 nm	Luo et al. (2014)
Te	*Aspergillus welwitschiae*	50 nm	Elsoud et al. (2018)

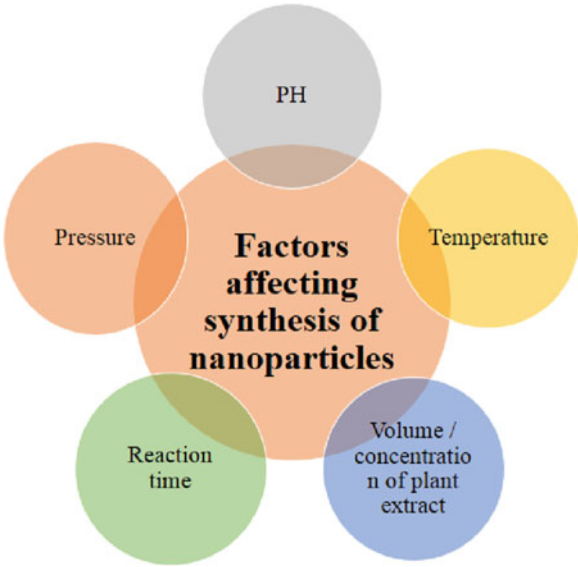


Fig. 3 Factors affecting synthesis of nanoparticles

3 Factors Affecting Biosynthesis of Nanoparticles

Numerous studies have been reported that changes in the environmental factor and reaction time affect the dynamic nature of synthesized nanoparticles. Manufacture or synthesis of nanoparticles is affected by several factors, as shown in Fig. 3.

3.1 pH

The pH of the medium plays a vital role in the process of nanoparticle synthesis. pH influences the synthesized nanoparticle's size, shape, and reaction time (Armendariz et al. 2004). pH can alter the electric loads of molecules that influence their ability to stabilize nanoparticles (Makeeva et al. 2014). In addition, nucleation center formation increases with increase in pH, which is directly proportional to the reduction of metallic ion to metal NPs. At the same time, the solution of pH also changes the activity of functional group present in the medium and, ultimately, affects the rate of reaction (Bali and Harris 2010). The study reported on Au nanoparticles synthesized by *Avena sativa* found that the size of nanoparticles was mainly based on the pH of the medium. It is shown that Au nanoparticles synthesized at pH 2 were observed having large sizes (25–85 nm) in small quantities. When pH was increased to 3 and 4, it formed smaller size nanoparticles in large quantities (Armendariz et al. 2004). A study on the effect of pH on the biosynthesis of Au nanoparticles by *Cacumen platycladi* leaf extracts found that the size of nanoparticles decreases at higher pH because the higher pH leads to a reduction rate of the chloroaurate ions, decreases the anisotropy growth, and increases the homogenous nucleation. Another study done on silver and gold nanoparticles by Jacob et al. found that at pH 3.3, Ag particles reduce slowly as compared to Au particles, while at pH 10.8, simultaneous reduction occurred in both metals (Zhan et al. 2011). Moreover, Soni and Prakash (2011) also reported that the size and shape of the Ag nanoparticle can be controlled via changing the pH of the solution.

3.2 Temperature

Temperature of the surrounding or the medium is also one of the important factors that affect the size, shape, and reaction time of synthesized nanoparticles. According to Sneha et al. (2010), formation of nucleation center depends on the temperature as it is directly proposal to the temperature. In addition, the temperature has a direct relation to the method used for the synthesis of the nanoparticles. Higher temperature is required in the physical method (>350 °C) while the chemical method required lower temperature than the physical method (<350 °C). Synthesis of green nanoparticles required ambient temperature or less than 100 °C (Patra and Baek 2014). Iravani and Zolfaghari (2013) attempted to investigate the influence of temperature by heating the reaction mixture of *Pinus eldarica* bark extract with $AgNO_3$ at different temperatures such as 25, 50, 100, and 150 °C, respectively. Results found by the authors were an increase in absorbance and a decrease in Ag nanoparticles while temperature increased. The authors also observed that at 100 °C little concentration of leaf (0.6 ml) was required, while at temperature 27 °C more concentration of leaf (2.5 ml) was required for biosynthesis of silver nanoparticles. In addition, it was found that nanoparticles that were produced at high temperatures were more stable but larger in size. Another study done by Sheny et al. (2011) investigated the process for reduction of Au and Ag ions at different temperatures by *Anacardium occidentale* leaf extract and standardized the most appropriate condition for bimetallic Au–Ag synthesis. This study also found that a higher concentration of leaf extract was required for synthesis of stable nanoparticles at lower temperatures as compared to higher temperatures.

3.3 Reaction Time

The quality and type of synthesized nanoparticles are greatly affected by reaction time or stirring time. Reaction time directly influences the stability, shape, and size of the synthesized nanoparticles (Darroudi et al. 2011).

The stirring time will allow the metallic salt to interact properly with the reducing agent present in the plant extract. Reaction time also depended on the concentration of reducing agent present in the extract or sample medium. In other terms, plants containing more amounts of secondary metabolites required less time and plants containing fewer secondary metabolites required more time to synthesize nanoparticles (Balavandy et al. 2014). Moreover, it is also reported that reaction time depends on other factors such as acidity and basicity of reaction mixture, temperature, reducing potential of the extract, enzymes, and light intensity (Kuchibhatla et al. 2012; Mudunkotuwa et al. 2012).

3.4 Pressure

Pressure applied to the reaction mixture is also one of the factors that affects the synthesized nanoparticle's size, shape, and stability (Pandey 2012). The rate of metal ion reduction using nanoscale particles of the biological agents was much faster at ambient pressure conditions (Tran and Le 2013).

3.5 Volume/Concentration of Plant Extract

Many studies have reported that the size, shape, and reaction time are directly linked to the quantity or volume of the plant extract taken for the synthesis of nanoparticles. For the synthesis of silver nanoparticles, effects of 1, 5, 10, 15, 20, and 100 ml leaf extracts could be tested. Since silver nanoparticle synthesis requires less volume, it is recommended to use 1, 2, 3, 4, and 5 ml for synthesis of Ag nanoparticles. However, the concentration of leaf extracts is significantly influenced by the content (phenol, tannin, polyphenol, and anthocyanin) of the extract as it is significantly contributing in the breaking down of Ag++ ions for the formation of stable Ag nanoparticles

(Lade and Shanware 2020). In the study on *Aloe vera* leaf extract done by Chandran et al. (2006) to modulate the size and shape of the synthesized gold nanoparticles, it was observed that maximum nanoparticles of gold were triangular in shape and their size ranged from 50 to 350 nm based on the concentration of extract used. Furthermore, addition of more concentration of the extract to an $HAuCl_4$ solution resulted in the formation of larger nano-gold triangles but the ratio of nanotriangles to the spherical nanoparticles was decreased when more amounts of extract were added.

4 Nanofertilizers: An Efficient Source of Crop Nutrient

Worldwide, agriculture systems are facing major challenges, which include reduction in yield, loss of agricultural land, lack of nutrient availability, less efficiency of nutrients, loss of organic matter, poor soil quality, and lack of accessibility of water. Producing enough food to feed the increasing population, which is expected to reach 9 billion by 2050, is becoming more difficult in this critical situation (Yuvaraj and Subramanian 2020). To meet the target of production, it is necessary to increase the production of agriculture. So, farmers are using chemical fertilizers, which provide the necessary nutrient to the plant and soil. Following the Green Revolution in India, consumption of chemical fertilizers such as urea, diammonium phosphate (DAP), and single super phosphate (SSP) increased by approximately 29% in order to meet the soil's shortage of N, P, and K. These fertilizers help to increase food production; however, besides its benefits, it has many harmful effects, as we know most parts of these chemical fertilizers are not available to the plant and are lost as volatilization and runoff. It is reported that after application of fertilizers, approximately 40–70% of N, 80–90% of P, and 50–70% of K are lost to the environment and cause pollution as well as contribute to global warming (Park et al. 2012). Nanotechnology helps to solve this problem by coating these fertilizers with nanomaterials. As the size of nanomaterials falls between 1 and 100 nm due to their nanoscale size, nanomaterials have completely different properties than the bulk that is being investigated for new agricultural opportunities. Nanoparticles help to improve crop yield by modifying the role of fertilizers. Different forms of NPs may be used as fertilizers or fertilizer carriers (Sindhu et al. 2021). Nanomaterial has the capability to slow the release of fertilizer as it has higher surface tension and holds more strongly from the plant. In addition, nanocoating helps to slow the dissolution of fertilizers, allowing it to be more effectively consumed by the plants and preventing excess fertilizer loss in the environment (Duhan et al. 2017). Nanofertilizer is economical, less environmentally harmful, and reduce the cost of fertilization with less fertilizer used than traditional fertilizer (Adhikari et al. 2014). In addition, nanotechnology is considered a new emerging science in the field of agriculture due to its application in nanofertilizers to improve crop yield or growth with minimum effect to the environment (Yuvaraj and Subramanian 2020). There are mainly three classes of nanofertilizers that have been proposed, as shown in Fig. 4.

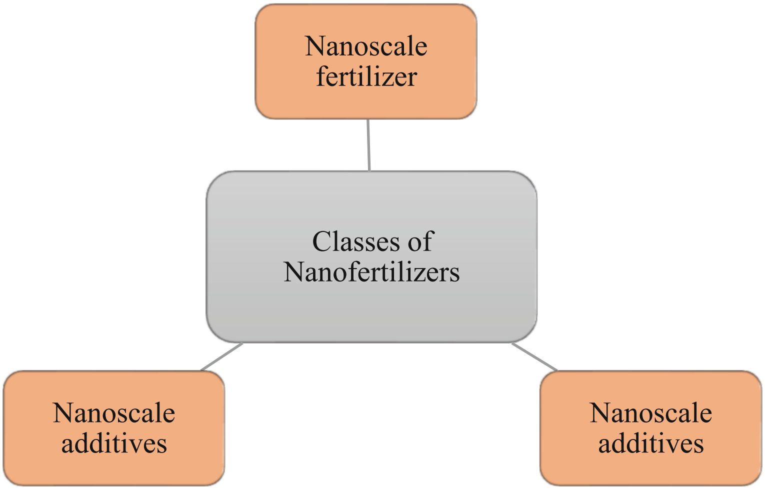


Fig. 4 Classes of nanofertilizers

Nanoscale fertilizer includes the nanoparticles, which contain the nutrient, nanoscale additives (traditional fertilizer along with nanoscale additives), and nanocoating (traditional fertilizer coated or loaded with nanoparticles) (Mikkelsen 2018). Moreover, conventional fertilizer is mainly applied in two ways, either by spraying or foliar application, which results in the loss of fertilizer without reaching the plant and soil, and hence repetition of this fertilizer is required. Nanofertilizers are mainly accomplished by the coating or encapsulation of fertilizers and by the slow release of nutrients or by controlling the water penetration into the fertilizer so that it reduces the loss of excess fertilizer. In addition, nanofertilizer optimizes the release of fertilizer according to the environmental conditions and plant's needs (Rakhimol et al. 2021). Nanoformulation helps to enhance the solubility of the nutrient constituents in water and that is why it enhances the accessibility of those nutrients to the plants. Moreover, the time of nutrient release could be extended by a controlled and slow release of nutrients from nanocarriers with no waste. The majority of them can provide nutrients to plants during their lives by adjusting the release profile according to the stage of development of the plants (Rakhimol et al. 2021). Previously, it has been also suggested that zeolite mineral, which is a naturally occurring nanoparticle, could be used in agriculture. However, nowadays synthesized nanoparticles with different chemical and physical properties suit a variety of applications in agriculture (Mikkelsen 2018). Some studies and patents strongly indicate that nanofertilizer formulation has a lot of scope for improvement in the agriculture system, as shown in Table 3. Foliar application of nanoparticles in the form of nanofertilizers increases the crop yield under arid conditions; a foliar application of 640 mg ha^{-1} nanophosphorus (40 ppm concentration) yielded about 80 kg ha^{-1} P, equivalent yield of pearl millet and cluster bean (Elizabath et al. 2019).

Table 3 Application of nanofertilizers on various crops

Nanofertilizer/ nanomaterial	Crop	Application	Reference
TiO_2	*Spinacia oleracea*	To enhance biomass accumulation, and nitrogen, protein, and chlorophyll content	Yang et al. (2007)
Nano-sized nutrients (ZnO and TiO_2 nanoparticles)	*Solanum lycopersicum*	To boost growth and antioxidant	Raliya et al. (2015)
Fe/SiO_2	*Zea mays*, *Arachis hypogaea*	In biomass accumulation and to increase plant growth	Najafi Disfani et al. (2017)
Nano chitosan NPK fertilizer	*Triticum aestivum*	To increase crop index, harvest index, and mobilization index	Aziz et al. (2016)
FeS_2	*Daucus carota*, *Brassica juncea*, *Spinacia oleracea*, *Cicer arietinum*, and *Sesamum indicum*	To enhance crop yield and germination	Das et al. (2016), Srivastava et al. (2014)
Application of nano-ZnO	*Spinacia oleracea*	To enhance leaf physical and nutritional properties	Kisan et al. (2015)
Nano-NPK fertilizer	*Oryza sativa*	To enhance growth and development, TPC, and antioxidant activity	Benzon et al. (2015)
Ag NPs	*Triticum aestivum*	To increase tolerance to heat stress and to enhanced growth	Iqbal et al. (2019)
Ag NPs	*Vigna sinensis*	To stimulate soil microbial diversity and increase growth in biomass	Mehta et al. (2016)
ZnO	*Coffea arabica*	To increase biomass accumulation, and enhance growth and net photosynthesis	Rossi et al. (2019)
ZnO	*Nicotiana tabacum*	To increase metabolites, enzymatic activity, and anatomical properties	Tirani et al. (2019)
CuO	*Spinacia oleracea*	To enhance photosynthesis and biomass production	Wang et al. (2016)

5 Nanopesticides: Controlling Plant Diseases

In agriculture, pesticides are widely used to protect crop against pests and diseases, resulting in the increased crop yield. Despite the fact that pesticides are highly efficient and safe means of pest and disease control, their use is not without risk. It

Table 4 Application of nanopesticides on various crops

Nanomaterials	Crop species	Pathogen/Disease controlled	Reference
ZnO, Ag NPs, and CuO	*Prunus domestica* fruits	Protect against gray mold caused due to *Botrytis cinerea*	Malandrakis et al. (2019)
Al_2O_3 NPs	*Solanum lycopersicum*	Suppress root rod	Shenashen et al. (2017)
Ag NPs	*Vigna unguiculata*	In vitro inhibition of *Xanthomonas axonopodis* and *Xanthomonas campestris*	Vanti et al. (2019)
CuO	*Solanum lycopersicum*	Suppresses the late blight disease occurring due to *Phytophthora infestans*	Giannousi et al. (2013)
MgO	*Solanum lycopersicum*	Suppresses pathogen *Ralstonia solanacearum*	Imada et al. (2016)
Silver-doped titanium oxide	Tomato, potato, apple	Controls diseases caused by *Fusarium solani* and *Venturia inaequalis*	Boxi et al. (2016)
Chitosan NPs	Chili seed	Show antifungal activity against *Rhizopus* sp. *Colletotrichum capsici*, *Aspergillus niger*, and *Colletotrichum gloeosporioides*	Chookhongkha et al. (2012)
Nanochitosan encapsulated in *Cinnamomum zeylanicum*	*Cucumis sativus*	Protects against *Phytophthora drechsleri*	Mohammadi et al. (2016)

has a number of negative consequences, including pollution of the soil and residual toxicity in food (Khan and Rizvi 2017). In addition, chemical pesticides are resistant to biodegradation, which affects soil microbes, pollinator insects, birds, fish, and humans. It is estimated that hardly 1% of the applied pesticide kills the targeted species, while 99% affects the non-targeted species that is beneficial to the soil and plant interaction (Gill and Garg 2014). Conventional practices involve high doses or use of a large scale of herbicides, insecticides, and fungicides but most of them are lost in the environment, which harms the microbial diversity in the soil as well as causes environmental pollution such as soil, surface water, and groundwater pollution. However, many studies have been shown that pesticides applied at a lower dose are safer for the environment. But, most of the pesticides are poorly soluble or insoluble due to their lipophilic nature and have strong intermolecular bonding or high lattice energy. Therefore, it requires large concentration and also requires repetition (Hayles et al. 2017). In this technological era, nanotechnology is an emerging technology that helps us to solve this issue by using nanopesticides or nanoformulations. Numerous studies have reported that nanomaterial was potential against the plant pathogens, as shown in Table 4. So these materials can be used in the preparation of the nanopesticides and nanoinsecticides, as well as they can be used as insect repellents (Sangeetha et al. 2017; Bhattacharyya et al. 2016; Prasad et al. 2017). Recently, scientists have been focusing on the research trend in which they decrease the particle size of existing pesticides to the nanoscale or encapsulate active ingredients in the nanoparticles. Nanoemulsions, which can be oil- or water-based and comprise pesticide nanoparticle suspensions, have a widespread application in pest and disease control. Because of the lower surface tension, they have more stability, increased leaf coating, and uptake via plant cell walls. According to Madbouly et al. (2017), nanopesticides avoid the use of toxic chemicals that trigger resistance or harm the environment. Nanopesticides may offer a control delivery system with greater effectiveness than a lower dose of pesticides (Perlatti et al. 2013). Nanoencapsulation of pesticides helps in the slow and controlled release of active ingredients, which reduces excess runoff of unwanted pesticides (Agrawal and Rathore 2014). Moreover, nanocarrier helps in site-specific or site-target delivery of pesticides for plant protection (Nair et al. 2010). In general, nanotechnology could be used for crop safety in two ways: Nanoparticles that are toxic to pests and pathogens that act as pesticide carrier, for example metal oxide nanoparticles such as ZnO, SiO_2, Cu, and TiO_2, protect the plant against microbial disease and control its activity. ZnO nanoparticles are reported for the antifungal and antibacterial activity that inhibits the human pathogens such as *Escherichia coli* and *Listeria monocytogenes*, and plant pathogens like *Penicillium expansum* and *Botrytis cinerea*. ZnO nanoparticles affect the cellular function of the fungi (Dubey and Mailapalli 2016). Lu et al. (2006) suggested that the TiO_2 photocatalysis technique is more effective than conventional fungicides to control litchi fungal disease. Mesoporous silica with gold nanoparticles can be used as a gene gun to deliver chemicals, nutrients, and protein directly into the plant (Torney et al. 2007). Another study demonstrates the Ag NPs can be used as potential inhibitors of the *Colletotrichum* spp. in cucumber and pumpkin field, and also found that Ag NPs are more effective than the bulk Ag treatment (Lamsal et al. 2011). Studies on copper nanoparticles found that Cu NPs have potent antibacterial and antifungal activities against a wide range of bacteria and fungi (Giannousi et al. 2013). El-Saadony et al. (2020) found that copper nanoparticles showed excellent insecticidal properties against the stored product pest *Tribolium castaneum*. Another way in which nanomaterials act as a carrier is through various nanoformulations such as nanoinsecticides, nanoherbicides, and nanofungicides. Nanoencapsulated pesticides have potential to target specific pest or insect so that it decreases the killing of the non-target organism as well as reduces the dose of pesticide. Nanopesticides have the ability to absorb on the plant surface, facilitating the prolonged or slow release of the pesticide than the conventional pesticide that washes out with rain (Scrinis and Lyons 2007). Wheat plants treated with nano-structured alumina significantly killed the two insect pest species *Sarocladium oryzae* and *Rhyzopertha dominica* (Stadler et al. 2010). Moreover, polymer-based nanoformulation has been used for the encapsulation of a wide range of insecticides, for example, nitrogen, starch, polyester, and alginates. In addition, other forms of polymer or non-polymer such as nanofibers, nanogels, nanosphere, micelles, and nanoemulsions have been used for the encapsulation of the insecticides (Shah et al. 2016; Mali et al. 2019). Chitosan and Cu nanoparticles combine to give antibacterial activity against the *Fusarium oxysporum* and *Alternaria solani* (Saharan et al. 2015). Another study was done by Kheiri et al. (2017) using chitosan NPs for their antifungal activity in wheat plants to protect against *Fusarium graminearum*. Nanoherbicides have the potential for targeted and concise delivery of herbicides for weeds, which reduces the continuous use of herbicides. Carboxy methyl cellulose (CMC) has been found to be one of the potential herbicides for future agriculture (Kumar et al. 2015).

6 Nanosensors: Detection of Plant Diseases

Nanosensors and nanobiosensors are among the most important tools for the management of the agricultural field and crop. Nanosensors are a type of analytical device having a dimension of 100 nm or less. It helps to monitor for the soil quality, crop health, crop improvement, pesticide and nutrient delivery, etc. (Ghormade et al. 2011). Nanobiosensors include the incorporation of biology and nanomaterial into sensors, which has opened up a new avenue for the precision, sensitivity, and rapid responses to detect impairments (Dubey and Mailapalli 2016). Nano-based sensors are very effective in terms of their sensing, monitoring, and detection. It allows the detection of the microbes, nutrients, biotic and abiotic stresses like drought and temperature, etc. (Malik et al. 2013; Omara et al. 2019). In nanosensors, nanoparticles or nanoemulsions are engineered in such a way that they trigger the chemical or electrical signal when it is exposed to the contaminant. The aim of nanobiosensors is the detection of the biochemical and biophysical indications linked with specific stress at molecular level. By the use of smart sensors in precision farming, farmers increase productivity and make better decisions with accurate information (Mali et al. 2020). Throughout the growing season, a nanosensor-based global positioning system (GPS) is used to monitor cultivated fields in real time. It can use wireless nanosensors for comprehensive monitoring of real-time crop growth (Panpatte et al. 2016). Nanosensors solve the issue of the shortage of irrigation water through the automation of irrigation system and also provide information about soil and water tension in real time, which maximizes the water efficiency (Fraceto et al. 2016). Furthermore, timely and accurate information on the insect or diseases will help us to timely use fertilizers and pesticides to shield crop from the infestation. For detection of insect attack, Afsharinejad et al. (2015) have developed a wireless nanosensor. This sensor is able to distinguish between the volatile organics released by several host plant species and the insect forms. Another study suggested that in the wheat plants for detection of Karnal bunt disease, nano-gold-based immunosensors can be used (Singh et al. 2010). In addition, scientists have reported that the development of bionic plant through injecting nanoparticles into the cell or chloroplast of plants for detecting objects in their environment has important potential in precision farming (Ghorbanpour and Fahimirad 2017; Kwak et al. 2017). Wang et al. (2010) suggested that a gold electrode modified with Cu nanoparticles helps in the detection of harmful fungal infestation by monitoring the level of salicylic acid in oilseed. The study of plant growth by regulation of growth hormones like auxin is done through multiwalled carbon nanotubes, which helps to find which marginal soil–plant root can easily acclimatize to their particular environment (McLamore et al. 2010). Ganeshkumar et al. (2016) suggested that potassium niobate nanofibers help to sense the humidity as it has a large surface-volume ratio. Many scientists also suggest that nanosensors, which are based on the deoxyribonucleic acid (DNA) detection technology through hybridization reaction, are used for detection of the genetically modified (GM) organisms in agricultural crops and genetically modified ingredients in food products (Manzanares-palenzuela et al. 2015). Undoubtedly, the intelligent use of nanosensors in agriculture system is a potential tool for ensuring long-term development by managing crop growth and soil health. However, the application of nanosensors especially in field studies is not sufficient yet, therefore it requires more research in this area. This area of research also opens up a new opportunity for a future scientist.

7 Challenges for Nanotechnology in Agriculture

Nanotechnology has enormous potential to make agriculture more proficient and resourceful. It enables precision farming by delivering nutrients, fertilizer, and pesticides in controlled manner and at a specific time. Nanotechnology also helps to improve the soil condition and in diagnosis of crop diseases at any stage. Although a number of reports are available on nanotechnology, it has tremendous benefits in the agricultural field. However, scientists have reported the preparation and properties of nano-agri-products, but the development and validation of these products for commercial use are mostly at an early stage. The concerns related to nanomaterial toxicity, transportation challenges, health hazards, and the incongruity of regulatory structure restrict the acceptance of adopting nanotechnology in agriculture (Pandey 2018). In addition, Oriakhi (2004) reported that customer perception and conviction about nanotechnology, social and cultural challenges, lack of collaboration among agencies, lack of targeted research projects, lack of financial resources, management challenges, and industry uncertainty about universities are all factors that hinder the agricultural commercialization of nanotechnology. Intellectual property also influences the commercialization of nano-agri-products. The topic of intellectual property rights, as with other rapidly evolving technologies, is important when contemplating commercialization. Problems may occur when the university or government researchers are perceived to be getting too close to industry "know-how," and when industry desires exclusive rights (Tegart 2001). According to a survey, the following five top obstacles to the commercialization of nanomanufacturing were identified by respondents (Soleimanpour et al. 2011): (1) high cost, (2) lack of investment capital, (3) lack of qualified manpower, (4) process scalability, and (5) the belief that nanotechnology takes longer time to reach the market. The advancement of nanotechnology also poses ethical concerns regarding its potential effects on human health and the environment. Nanotechnology provides numerous benefits while also posing new difficulties to environment and human well-being, as the nanomaterial has completely different properties than bulk materials, which may have negative consequences. For instance, nanoparticles have the same dimensions as some biomaterials, which may cause new health problems by interfering with the physiology of human and environmental species through various processes (Purohit et al. 2017). Nanomaterials' effects on the environment and human health are still not fully known. The health and environmental concerns presented by nanomaterials are difficult to measure due to their various features and behavior. Because the kinetic (absorption, distribution, metabolism, and excretion) and hazardous properties of the materials are controlled by their charge, shape, and size, even nanomaterials of the same chemical composition with various sizes or shapes may have drastically varying toxicity (Pragya et al. 2012). The nanotechnology practice in agriculture is concerned about the accumulation of nanomaterials and their potential entry into the food chain (Priester et al. 2012). The plant is a vital component of all ecosystems, and in the environment they play an important role in the fate and carrying of synthesized nanoparticles through plant absorption and bioaccumulation in the environment. Bioaccumulation, biotransformation, and biomagnification of nanoparticles in the food crops are even now not well defined. A very less number of reports are available on nanoparticle accumulation in plant species and its subsequent availability in food crops (Agrawal and Rathore 2014). This is also one of the key challenges to the commercialization of nanotechnology in agriculture. In addition, the major driving force for agricultural productivity is the plant–soil interaction, which is determined by any change in the physicochemical parameters of the soil profile. Moreover, the soil is the primary source for releasing the nanoparticles; thus their subsequent contact by various soil constituents may have a significant impression on the density, transport, and activities of NPs. Few studies on silver nanoparticles have reported the role of soil pH, organic matter (OM) content, and cation exchange capacity (CEC) in determining their destiny, toxicity, and bioavailability (Benoit et al. 2013; Shoults-Wilson et al. 2011). A low range of soil pH, OM content, and CEC has been shown to impede Ag sorption to the soil, resulting in an increased risk of Ag NP mobility, toxicity, and bioavailability. On the other hand, Ag sorption to the soil is enhanced by a higher pH range in the soil, cation exchange capacity, and organic matter content, which prevents Ag NP mobility, bioavailability, and further toxicity (Klitzke et al. 2015; Schlich and Hund-Rinke 2015). Therefore, it is consequently necessary to quantify the expected amounts of manufactured nanoparticles that may be present in the air, water, and soil before toxicological findings. Consider how humans approach the problem. Populations may be exposed to man-made nanoparticles soon and in the present (Agrawal and Rathore 2014). Because the use of nanotechnology in agriculture field is still in its initial stages, resulting in an unfavorable view, there is reluctance to accept this technology; the same was seen with genetically modified (GM) food crops, and it may be repeated, specifically in the European Union region (Mwaanga 2018).

8 Conclusion and Future Prospect

Undoubtedly, agrochemicals such as pesticides, fertilizers, and insecticides have significantly contributed to agricultural development and expansion. Despite the fact that agrochemicals provide significant benefits in terms of greater agricultural output, their excessive usage has resulted in serious problems for the environment and human health. Only a small portion of this agrochemical is consumed by plants while the rest are lost in the soil. Most of these agrochemicals are not easily degradable and their residue has been observed and measured in the majority of food crops; also, high amounts of nitrate and phosphate from chemical fertilizers have been found in both surface and groundwater resources. To solve this problem, advanced technologies such as the nano-enabled solution will be a crucial instrument in the next agri-tech revolution, which will make it more efficient, resilient, and sustainable. As discussed earlier, plenty of nano-agri-based products are available in the market, which includes nanopesticides, nanofertilizers, and nanosensors. The implication of this product in farming has several advantages such as increased fertilizer efficiency, better pest management, lesser chemical contamination, and, more importantly, lesser chance for the agricultural operators to come in direct contact with the hazardous material. Despite enormous advantages and significant impact on transferring the technology to the agriculture field, some constraints reduce its universalization. As per the public point of view, use of nano-based agri-products has a number of hazards; it has ethical problems and various uncertainties. The key reasons why the use of nanotechnology in agriculture is lesser than in other fields are: lack of knowledge, lack of infrastructure, lack of unifying regulation and guidelines, and environmental challenges. To popularize the use of nano-agri-based products in agriculture, several key steps need to be taken and a promising application of nanotechnology in all fields must be ignored; however, simultaneous risks on environment and human health must be considered. At the same time, the need of the hour is to move forward and make significant efforts in developing advanced studies focused on identifying knowledge gaps. In this regard, we propose that future research should focus on identifying alternative ways to avoid the risk associated with nanoparticle use. There is a need of validating the dose of nanoparticles under the safety limits and it should be clearly explained. To achieve a thorough understanding of nanotechnology, it must include full life-cycle assessment of nanoparticles' effect on each tropical level. Overall, we strongly encourage eco-friendly or green synthesis approach for nanoparticle synthesis, a method of biosynthesis that affects the toxicity of nanoparticle, and future studies that illustrate new applications in agriculture.

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Interaction Between Nanoparticles and Phytopathogens

Shakti Prasad Pattanayak, Pritha Bose, and Priyashree Sunita

1 Introduction

Phyto-diseases may evoke extensive deterioration in the plant community. It is crucial that phyto-diseases are rapidly identified and treated rationally. As per the current projections, the production demand for food globally needs to be doubled by 2050 (Tilman et al. 2011). With the anticipation that the changes in climate may contribute to disrupt the cycle of food production, such concerning prediction becomes more distressful. The plant pathogens are often greatly responsible for the annual loss of economically important plants and crops. In order to overcome this dire situation, nanotechnology extends its opportunities as a new edge weapon to improve and maintain plant health. With its diversified applications, the field of nanotechnology, specially nano-agriculture holds promise to provide us new avenues and streamline the utility of nanomaterials in crop production as well as protection of plants. Although the use of nanotechnology for phyto-disease management or diagnosis is at infancy, still it has tremendous potential in improving already existing as well as future crop production via plant protection techniques that will resist pests and diseases, help in phytopathogen monitoring, and plant diseases detection. However, there is still a lack of awareness and appropriate knowledge on how to bridge nanotechnology with agriculture and plant physiology and utilize it

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directly or indirectly in plant disease management. Thus, in this chapter we will discuss in detail the plant pathology and intertwined mechanisms along with the microbial organisms associated with it. Successively, new advancements and achievements acquired by utilizing nanotechnology in the field of phytopathology and agriculture will also be discussed for readers to gain insights into the role of nanomaterials in plant pathology.

2 Phytopathogens

A plant or phyto-disease can be broadly defined as any circumstance that evokes cascade of responses in plant cells and hinders the plant to perform its activity in highest potential. These diseases can be both biotic or abiotic in nature and the science of deciphering various phyto-diseases along with their causes is known as *plant pathology*. Plant pathology is closely related to bacteriology, virology, mycology, entomology, and weed science owing to the derogatory consequences of bacteria, virus, fungus, insects, and weeds, respectively, upon plants. Classification of plant diseases can be based on several criteria such as infected organs, disease symptoms, types of infected plants, or the causative phytopathogens. However, the phytopathogenic-based classification is considered to be more rational as it helps in easy determination of plant disease causes, related complications and probable measures of control (Cramer 1967). Following this criterion, phyto-diseases can be of two broad types: namely, biotic or infectious disease caused by microorganisms and abiotic or non-infectious disease which is the outcome of extreme environmental conditions (Horsfall and Cowling 1980). The diseases caused by abiotic factors, although being common, do not spread from plants to plants. Abiotic stresses include conditions such as excessive or deficient nutrients and moisture, soil compaction, presence of toxic chemicals in soil or air, salt injury, ice-attack, sun-scorch, etc. (Horsfall and Cowling 1980).

On the other hand, pathogenic microorganisms are the causative agents for biotic stress. The pioneering research indicating *Erwinia amylovora* for causing blight in pear and apple served as the foundation of plant pathology (Glawe 1992). With progress in time, several plant diseases due to bacteria, viruses, fungi, nematodes have been documented till then (Fang and Ramasamy 2015). Plant disease epidemics (epiphytotics) are also known to occur in many plants worldwide (Agrios 1997). The infectious disease occurs due to the phytopathogens' capability to get transferred from an infected to healthy plant resulting in identical disease as well as symptoms. While the internal plant environment is preferred for inhabitation by many phytopathogens, certain other microorganisms like bacteria and fungi live on the surface of plants. Some phyto-diseases also develop due to parasitic higher plants that grow upon attachment to other plants contributing to no mutual benefit but depriving the host plant of essential nutrients. This abnormal alliance leads to fragility of the healthy host plants. Examples of such plants are dodder, mistletoe, and witchweed broomrape.

2.1 Broad Classification of Phytopathogens

As discussed earlier, pathogens affecting plant health may vary from fungi, viruses, bacteria, parasitic higher plants, mollicutes, parasitic green algae, nematodes, protozoa, and viroids. Owing to their effective penetrating ability in plant tissues, these parasites can also tolerate diverse host conditions which enable them to feed and thus proliferate in plant tissues. Such pathogens which depend on living hosts for survival are known as obligatory parasites. On the contrary, the non-obligate parasites like fungi and bacteria can survive on both living and non-living hosts and utilize different nutrient media. Among the non-obligatory parasites, those who can grow/ develop on organic dead matter saprophytically are called facultative saprophytes (semi-biotrophs) (Ellingboe 1968). Another variety of facultative parasites (necrotrophs) which grow saprophytically in general can attack and cause disease in living plants but under certain circumstances. It has to be noted that severity in phyto-disease is not often dependent on the parasitism type or degree. For instance, weak parasitic pathogens are often responsible for greater derogatory outcomes in plants with respect to those caused by other obligate parasites. In most cases, the non-obligatory parasites use lysozymes for degrading plant cellular wall that allows progressive invasion as well as infection (Dollet 1984). The most common variants of pathogenic microorganisms that are responsible for diversified plant disease along with their characteristic features have been enlisted in Table 1.

The parasitic phytopathogens also possess negative impact on host metabolic processes. Vascular pathogens attack the xylem and phloem vessel tissues of host plants for their growth and multiplication processes that impede sugar and water transportation in host plant cells (Abdulkhair and Alghuthaymi 2016a). Phytopathogens (e.g., *Fusarium oxysporum f. sp lycopersici*, *Verticillium albo-atrum*, *Verticillium dahliae*, *Xanthomonas oryzae pv. oryzae*, *Ralstonia solanacearum*, *Xylella fastidiosa*, *Xanthomonas campestris pv. campestris*, *Erwinia amylovora*, *Clavibacter michiganensis ssp. michiganensis*) categorized as vascular wilt pathogens are responsible for overwintering soil along with plant debris (Yadeta and Thomma 2013). While most bacteria and fungi belong to groups of soil-borne microscopical pathogens, foliar pathogens are constituted of phyllosphere viruses, bacteria, and fungi. Spots, cankers, blights, overgrowth of plants, tissue rots, root branching, stunting, and leaf epinasty are some of the well-known and familiar plant disease symptoms (Martins et al. 2018).

Table 1 Common phytopathogens and associated plant diseases

Sr. No	Types of phytopathogens	Characteristic features	Top 10 economically important phytopathogens	Few common Plant Disease
1.	Bacteria	Microscopic (single-celled) organisms possessing cell walls. Mode of reproduce involves binary fission. phytopathogenic bacteria Most of the phytopathogenic bacteria among the 200 variants either grow as parasites within or on the surface of the plant or in plant debris or soil like saprophytes	*Pseudomonas syringae*, *Ralstonia solanacearum*, *Agrobacterium tumefaciens*, *Xanthomonas oryzae*, *Xanthomonas axonopodis*, *Xanthomonas campestris*, *Erwinia amylovora*, *Xylella fastidiosa*, *Dickeya (dadantii and solani)*, *Pectobacterium carotovorum* (Khater et al. 2017)	Aster yellows, bacterial wilt, blight fire blight, rice bacterial blight, canker, crown gall, basal rot, scab
2	Fungi and fungal like organism	These pathogenic species lack chlorophyll and thus are incapable of making their own food. They exhibit filamentous growth and reproduction may be dependent or independent on spores. These microorganisms are classified as necrotrophic, hemibiotrophic, and biotrophic based on their living styles or mechanism of interaction with host plants	*Magnaporthe oryzae*, *Botrytis cinerea*, *Puccinia* spp., *Fusarium graminearum*, *Fusarium oxysporum*, *Blumeria graminis*, *Mycosphaerella graminicola*, *Colletotrichum* spp., *Ustilago maydis*, *Melampsora lini*, *Phakopsora pachyrhizi*, *Rhizoctonia solani* (Dean et al. 2012)	Anthracnose, black knot, blight (chestnut blight, late blight), canker clubroot, damping-off, Dutch elm disease, ergot, Fusarium wilt, leaf blister, downy mildew, powdery mildew, oak wilt, etc.
	Virus and viroids	Viruses are characterized as intracellular particles bearing nucleic acid and are known to possess a protein coat that contributes in their different replication processes in the target living host cells. Virus-like particles devoid of protein coat are called viroids	*Tobacco mosaic virus*, *tomato spotted wilt virus*, *tomato yellow leaf curl virus*, *cucumber mosaic virus*, *potato virus Y*, *cauliflower mosaic virus*, *African cassava mosaic virus*, *plum pox virus*, *brome mosaic virus*, *potato virus X* (Scholthof et al. 2011)	Curly top, mosaic psorosis, spotted wilt
	Nematodes, *Phytoplasmas*	The microscopical worm like animals	–	–

(continued)

Table 1 (continued)

Sr. No	Types of phytopathogens	Characteristic features	Top 10 economically important phytopathogens	Few common Plant Disease
	and Parasitic higher plants	that are majorly characterized as soil dwellers are known as nematodes. Phytoplasmas are on the other hand bacteria like filamentous microscopic living organisms without cell walls. Parasitic high plants are chlorophyll containing plants that lack the ability to synthesize their own food and thus show parasitic activity on other host plants to collect water and nutrients		

3 Plant–Pathogen Interactions

3.1 The Disease Triangle of Host, Environment, and Pathogen

One of the most common models for studying plant pathology is represented by a triangle comprised of 3 major participants-host, environment, and pathogen (Fig. 1a). This model is based on the concept that a susceptible host can be attached by a biotic agent, that is, any virulent pathogenic microorganisms that give rise to disease. Thereby, elimination in any one of the factors may prevent disease development (Francl 2001). Such conditions can further promote the infection-inducing properties of opportunistic fungi and bacteria (Abdullah et al. 2017). As discussed earlier, phytopathogens possess the aptness for epiphytic survival or growth within tissues of host plants, soil and/or separate plants. Physical injury or weakness caused in plants by the hostile abiotic (environmental) factors further assists pathogenic entry into host cells. For instance, factors like temperature, excess or scarcity of nutrients, moisture, humidity, torrential rain, and imbalance in salinity help the pathogens to multiply as well as propagate within the host plant escalating the disease and thereby affecting the plant health adversely (Agrios 1997). It has been observed that favorable climate during the monsoon triggers disease epidemics such as pomegranate blight caused by bacteria expands exponentially under conditions of elevated humidity common in rainy season (Chikte et al. 2019). Moreover, both epiphytic and endophytic phases have been documented in life cycle of

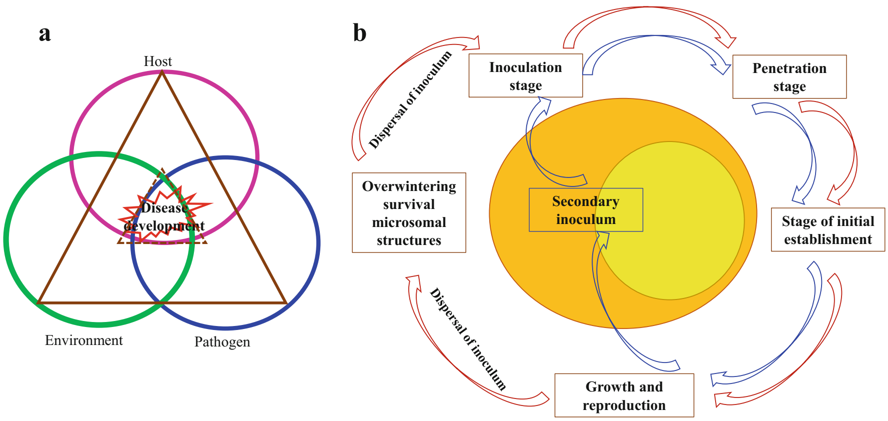

Fig. 1 (**a**) The vicious disease triangle of host, environment and pathogen: the phytopathogenesis only develops when each factor coincided with each other. (**b**) the cycle of disease development: the monocyclic virulent pathovars complete their cycle following the red arrows, while the polycyclic pathogenic microorganisms normally follows the blue arrows to complete their cycle for most of the seasons but shifts to the red arrows at the end

gram-negative pathogenic bacteria (Agrios 1997). The capability of phylogenetically rare species to elude disease pressure is well known and the host's phytogenic structure also modulates pathogens' potency to spread, thereby affecting disease severity (Gilbert and Parker 2016). Thus, knowhow of phylogenetic connection in host and also virulent pathogens serve in predicting disease risk in multi-cropping system, which may help to avoid probable economic loss. However, it is important to note that there are multiple variables within the three components of disease triangle that may alter both disease incidence and severity. Life cycle, genetic diversities, and biology of both plants and pathogens as well as environmental conditions are a few of such variables.

3.2 Disease Cycle

For disease development, the tissue or cell of host plant should be successfully invaded by a virulent pathogen. Fig. 1b depicts the series of events involved in development of phyto-diseases. A disease cycle can be monocyclic or polycyclic. The various stages of the disease cycle are being briefly discussed below (Abdulkhair and Alghuthaymi 2016b):

Inoculation This step involves the phytopathogen introduction into host. Different pathogenic microorganisms deploy different modes of inoculation and are also equipped with diversified specialized mechanisms that promote inoculation. While some pathogenic fungi use spores that are airborne for inoculation in addition to sclerotia of mycelium fragments, intact cells also represent the inoculum in cases of bacteria, protozoa, mollicutes, viruses, and viroids. The inoculum categorized as primary and secondary causes respective phyto-infections.

Penetration While certain plant pathogens utilize wound or injury sites and naturally occurring plant openings (stomata and hydathodes) to enter the host plant tissues, other pathogens employ unique modes to penetrate directly. Under optimum temperature, moisture and other favorable environmental conditions, fungi and nematodes undergo active penetration in tissues and cells of host plant.

Infection After invading the plant tissues, the phytopathogens develop a parasitic relation with the plant. Being unable for active penetration into the host plant tissues, phytoplasmas, bacteria, and viruses depend on alternative methods for infecting tissues and cells in plants. The virulent pathogens rely on insects as vectors that assist inoculation as well as dispersal.

Incubation After entering the plants, the pathogenic microorganisms enter the incubation stage and stay in latent condition for a specific period of time before initiation of the phyto-diseases.

Reproduction Depending on the type of phytopathogens, the mode of reproduction may be sexual of asexual.

Survival The evolution process of phytopathogens has enabled them for prolonged survival by tolerating hostile environmental conditions. The dark brown colored spores produced by fungal pathogen are an example which lower the light penetration and thereby prevent cell death. Another example of survival strategy may be the habit of soybean cyst nematode laying its eggs in a cuticle case. Such casing is very rigid that prohibits penetration of harmful chemicals or microbes which kill the eggs prior to hatching.

As discussed above, disruption in one or more steps of the cycle will either curb the disease severity or may even prevent its promotion or development in host plants. Thus, the knowledge of disease cycle may help to manage various phyto-diseases.

4 Phyto-pathogenesis-Linked Molecular Mechanisms Mediated by Bacteria, Viruses, and Fungi

Phyto-pathogenesis exhibits a critical and complicated process (Fig. 2a). As a pathogenic virulent microorganism encounters a plant, it should be capable enough for adapting to the living conditions in epiphytic surfaces as well as survive for adequate time period necessary for initiating infection. Thus, throughout the process of infection, the response toward environmental conditions plays a pivotal role. The correlation of signaling pathways (both intracellular and community level) with that of environmental signals triggers responses critical for phytopathogen populations. The ultimate goal of phytopathogens is to migrate from surface of the epiphytes into

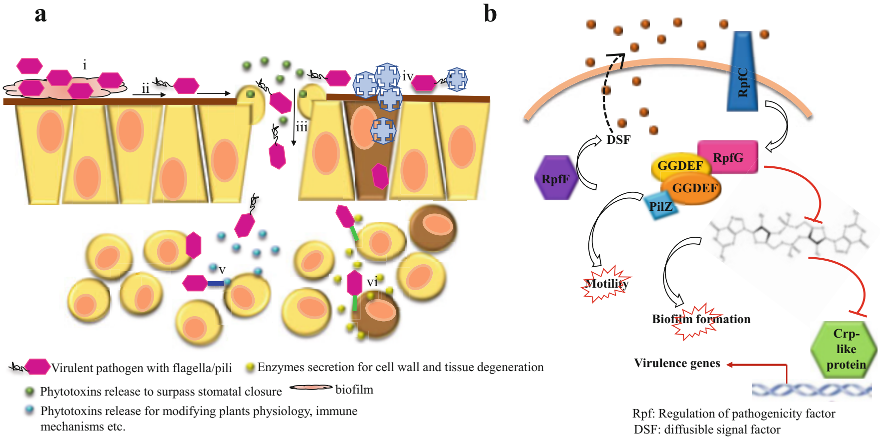

Fig. 2 (**a**) Basic mechanism of phytoinfection by pathogenic microbes: The common steps include (1) surface infestation and adaption of microbes along with formation of biofilm, (2) surface migration of the pathogens mediated by flagella/ pili to gain access through the apoplasts, (3) phytotoxin mediated stomatal entry, (4) damage of plant surface through ice nucleating agents (INA), (5) toxins mediated alterations of plant physiology essential functions and even immune responsiveness, (6) plant tissue degradation and disruption of cell wall through secreted enzymes. (**b**) Rpf conjugated QS/cdG signaling system in pseudomonas species: The sensor kinase, Rpfc upon sensing QS signal (DSF) produced by RpfF, causes phosphorylation and activation of RpfG. RpfG in turn via its phosphodiesterase activity degrades cdG thus reducing biofilm formation and Clp protein release repression. Subsequently, virulent genes undergo Clp mediated transcription. Additionally, interaction of RpfG with other GGDEF domain comprising proteins, is responsible for controlling bacterial motility. *Rpf* regulation of pathogenicity factor, *QS/cdG* quorum sensing/ cyclic di-guanosine monophosphate, *Clp* Crp-like protein

the host plant tissues mediated by motility or chemotactic pathways. This migration involves introduction into plant apoplast after surpassing the physical along with chemical barriers. Following their introduction in plant tissues/cells, phytopathogens utilize an array of effectors (proteins) and phytotoxins produced by different secretory systems that co-ordinate various pathogenic functionalities (Melotto and Kunkel 2013).

4.1 Bacterial Phyto-pathogenesis

4.1.1 Surpassing Stress on Epiphytic Plant Surface

The surface of leaves presents a hostile environment for virulent pathogens. Bacteria have to face regular exposure to desiccation, adverse alteration in temperature, UV radiation, and mechanical abnormalities like strong wind. Despite these hindrances, epiphytic bacteria possess certain virulence strategies that promote their microbial persistence on the surface of most plants. The epiphytic survival is materially regulated by metabolic responsiveness to shock, cold, stress, and desiccation (Djonovic et al. 2013; Freeman et al. 2013). In *Pseudomonas syringae (P. syringae)*, trehalose (osmo-protectant) has been indicated for benefiting its survival and also maintain its required population in phyllosphere (Freeman et al. 2010). It has also been suggested to potentiate nitrogen requirement and enhance proliferation in leaf apoplast thus contributing to plant disease development by *P. aeruginosa* (Djonovic et al. 2013). Various literatures have pointed out the pivotal contribution of exopolysaccharides (EPS) like alginate, xanthan, levan (Freeman et al. 2013; Dunger et al. 2007) in the epiphytic survival of various plant-related microbiomes such as *xanthomonas specie*s (Dunger et al. 2007) and *P. syringae* (Yu et al. 1999). The EPS molecules are closely correlated with epiphytic survival and contribute to enhance the pathogenic capability for resisting freeze-thaw process (Wu et al. 2012), tolerate stress due to osmosis and dryness (Freeman et al. 2013), and also maintain adequate microbial population (Dunger et al. 2007). Various phytopathogens possess the EPS molecules that mediate Ca^{2+} signaling quenching at the time of phyto-immune response and thereby allow the microbes to evade the immune system (Aslam et al. 2008). Relative to surface of leaves, literature points out strong upregulation of biosynthetic locus of levan in *P. syringae* pv. *syringae* (Pss) B728a in the apoplast that indicates its role in post-infection virulence (Yu et al. 1999). Moreover, the pathogenic trait of EPS molecules has also been observed in case of biofilm formation by Psa NZ V-13 (Renzi et al. 2012). On the other hand, Wss (acetylated cellulose) molecules not only foster the root colony formation of *Pseudomonas fluorescens*, but also facilitates *P. syringae pv. tomato* (Pto) DC3000 (Gal et al. 2003).

4.1.2 Signaling Cascades Regulated by Phytopathogens

The virulent phytopathogenic bacteria demonstrated evolved and efficient cell-to-cell signal transduction system which exhibits diversified and overlapping parallel input signals along with gene (non-linear) co-ordination. Moreover, the plant surface also reveals various bacterial species to be closely interlinked with various signaling systems. Among the wide variety of signaling systems QS (quorum sensing) and cdG (cyclic guanosine 3’,5’-monophosphate) signaling (second messenger pathway) are considered to perform major roles in plant pathogens.

4.1.2.1 Quorum Sensing (QS) in Phytopathogenic Bacteria

QS is utilized by ultraviolet bacteria for communicating as well as assessing cellular density via the products of autoinducers which are tiny signaling molecules. The major signals in bacteria are acyl-homoserine lactones (AHLs), DSF(diffusible signal factor), and Ax21.

QS molecules are majorly constituted by AHLs. AHL itself plays as pivotal role in positively regulating synthase gene transcription. *P. syringae* is known to produce

3-oxo-C6-HSL (homoserine lactone), an AHL molecule. In Pss, both synthesis of EPS and motility are controlled by ahlI/ahlR system which are essential for maintaining virulence of pathogenic bacteria as well as plant colonization (Quinones et al. 2004, 2005). While *Agrobacterium tumefaciens* (crown gall bacteria) control virulence by producing 3-oxo-C8-HSL that stimulates Ti plasmid copy numbers, secretion of phytotoxin and flagellum assembly coordinated motility in *Burkholderia glumae* (rice pathogen) is regulated by C8-HSL production (Kim et al. 2004). LasI/LasR, OscR (orphan regulator), and RhlI-RhlR are 3 AHL pathways which are employed by *P. aeruginosa* for producing 3-oxoC12-HSL along with C4-HSL that are known for affecting more than 300 gene expressions among which many are associated with restriction of toxins, biofilm formation, and also motility (Schuster et al. 2003). Another QS molecule called PQS (Pseudomonas quinolone signal), chemically known as 2-heptyl-3-hydroxyl-4-quinolone, is also reported to be synthesized by *P. aeruginosa* which control both formation of biofilm and virulence factors production (Allesen-Holm et al. 2006). Moreover, PQS, las, and rhl (complete and semi-independent) QS systems also mediate LasB expression encoding a secreted (type II) protease.

Recently, another QS signal known as Ax21 has gained quite interest. *Xanthomonas oryzae pv. oryzae* produces the Ax21 which is a sulfated small protein in nature and performs the role of QS molecule necessary for expressing virulence genes (Han et al. 2011). *X. oryzae pv. oryzicola* (Qian et al. 2013) and *Stenotrophomonas maltophilia* (McCarthy et al. 2011) have been documented to possess similar proteins that are interrelated with EPS and biofilm formation enhancing motility and virulence.

Another essential QS molecule termed as DSF is composed of fatty acids (unsaturated). cis11-methyl-dodecenoic acid is a DSF signal that is recognized by pathovar Xcc responsible for causing crucifer black rot (Wang et al. 2004) and is involved in modulating virulence as well as synthesis of xanthan and protease (Barber et al. 1997). DSF has also been reported to be used by *Xy. Fastidiosa*, *X. oryzae pv. Oryzae*, and other Xanthomonas species. DSF signaling pathway which is synchronized by components of the gene cluster Rpf (regulation of pathogenicity factor) present in Xcc upon mutation reduces virulence (Barber et al. 1997). DSF upon synthesis is readily detected RpfC, a component of RpfC/RpfG (hybrid sensor kinase) which is also known for negatively regulating DSF synthesis (Slater et al. 2000). Following activation of RpfC/RpfG system and signal transduction through it, cdG is degraded with subsequent repression of Clp (Crp-like protein) transcription regulator release that finally leads to activation of virulence gene expression (Fig. 2b) (Chin et al. 2010). Xcc also consists of another DSF sensor, RpfS apart from RpfC which has been proven to be essential for virulence in Chinese radish (An et al. 2014a). On the other hand, mutation of RpfF in *Xylella fastidiosa* increases colonization and virulence in grape xylem tissues. *Xy. fastidiosa* engage DSF signal transduction in a multifaceted fashion for regulating its colonization, virulency as well as adhesion potential (Chatterjee et al. 2008a, b).

4.1.2.2 cdG Signal Transduction Pathway

Cyclic adenosine monophosphate (cAMP) and cdG (cyclic-di-GMP) like nucleotides that serve as secondary messengers, function as signaling molecules with pleomorphic roles for controlling and regulating virulence of bacteria. Apart from regulating virulence, cdG the secondary messenger participates in coordinating a wide range of functions including motility, biofilm formation. PDE (Phosphodiesterase) and DCGs (diguanylate cyclase) are known for regulating intracellular levels of cdG. While DGCs utilize 2 GTP (Guanosine triphosphate) molecules for synthesizing cdG, PDEs cause degradation of the same. Often additional domains such as GAF, REC, or PAS present in DGC/PDEs are also associated with signaling. cdG interacts with a wide variety of binding domains for exerting its action, some of them being PilZ domain containing protein, DGCs, and PDEs which are enzymatically inactive, transcriptional regulators such as Clp, RNA riboswitches, and FleO (regulator of pseudomonas motility and/or EPS) (Romling et al. 2013). cdG in DSF/rpf signaling system undergoes interaction with Clp preventing its promoter binding and subsequent related target genes transcription (Fig. 2b). Clp in Xanthomonas species controls gene expressions that encode extracellular enzymes (Chin et al. 2010). Similar Clp/cdG interaction is evident in *Xanthomonas axonopodis pv. Citri* (Leduc and Roberts 2009). On the other hand, Xcc also exhibits a different dual component RavS/RavR system which is associated with cdG and found to be important for bacterial virulence. This RavR protein is involved in alteration of cdG levels mediated by activity of PDE via its EAL domain and also modulates expression of virulence factors through Clp, the transcriptional regulator (He et al. 2009). The regulatory effect of cdG systems in controlling multiple and essential behavioral facets of phytopathogenic Pseudomonas species along with regulating the virulence of various other pathogenic species and pathovars is well documented (Pfeilmeier et al. 2016). Previous literatures also indicate its role in managing activity of T3SS (type III secretion system) and flagellum with simultaneous regulation of proteome composition by modifying ribosomes (Trampari et al. 2015; Little et al. 2016). It has been suggested that Gac/Rsm nexus that is responsible for controlling quantum signaling, biofilm formation, secretor systems, toxin, and siderophore production, manipulates productions of PDE/DGC thereby subsequently affecting cdG levels (Moscoso et al. 2011, 2014). While expression of T6SS (type IV secretion system) is interlinked with GacA (sensor kinase) in *P. syringae* (Records and Gross 2010), RsmA, the post-transcriptional regulator (RNA binding), when trans-overexpressed results in repression of secretion of various virulence factors (Kong et al. 2012). The key functionalities of cdG signal transduction in *Ralstonia solanacearum*, Serratia, and Erwinia genera need to be elaboratively explored apart from Xanthomonas and Pseudomonas and species. Recently researches have revealed two new targets for cdG binding in XCC and *P. syringae*, which are XC_3703 (YajQ family protein) (An et al. 2014b) and injectisome (type III) ATPase HrcN, respectively (Trampari et al. 2015).

4.1.3 Adapting Skills of Pathogenic Bacteria to Phyto-environment

The interaction and cross talk between different components of plant microbe are known to largely affect phytopathogenic bacterial behavior in natural environment. Epiphytic endurance and phyto-infections are affected prominently by both commensal and antagonistic interactions (Delmotte et al. 2009; Ritpitakphong et al. 2016). Downstream of the signal transducing nexus, pathogenic responses are integrated to environment by transcriptional alterations related with life on phyto-surfaces. It has been documented that in Pss B728a (*P. syringae* strains) affecting the bean plants' surface, there is marked upregulation of genes associated with nutrient attainment, virulence, intracellular signaling as well as membrane transport (Marco et al. 2005). On the other hand, epiphytic survival of Pss B728a on surface of the leaves is promoted by active and strong induction of osmotolerance coupled with T6SS and alginate synthesis. Another phyto-environment identifying regulatory pathway in Ag. tumefaciens involves low pH, plant-related sugars, and phenolics (acetosyringone) mediated evocation of virulent gene expression (Peng et al. 1998). In Agrobacterium, certain chemical signals-mediated induction of virulence gene at the site of plant wounds are modulated by VirAG/ChvE pathway that finally results in effective crown gall tumor formation (Peng et al. 1998).

4.1.4 Apoplastic and Plant Surface Motility of Bacteria

Motility or migration plays an important role in phyto-infections. Recently, regulation of motility as well as pili, surfactant or flagella loci expression at proper time during phyto-infection phases are being considered as one of the salient factors in pathogenicity of plant. When in contact with surface of leaves, many phytopathogenic bacteria express traits that assist in promoting bacterial persistence until apoplastic penetration is allowed by environmental conditions. Under favorable conditions, pathogens utilize different motility systems that enable their migration from surface of the leave to interior of the plants through different access sites like wounds and stomata. Flagellar motility confers epiphytic competence benefit in *P. syringae* and plays an important role in plant virulence and surface colony formation (Tans-Kersten et al. 2001). It has been observed that chemotaxis along with formation and utilization of surfactant molecules in bacteria are closely intertwined with expression of flagellar genes that allow bacteria for migration through leaf surfaces (Yu et al. 2013; Burch et al. 2012). Signaling genes like rpfS (in Xcc) (An et al. 2014a), rimK (in *P. syringae*) (Little et al. 2016), and xbmR (from *X. citri* ssp. *Citri*) (Yaryura et al. 2015) upon deletion contribute in defective bacterial virulence. Also. in *P. syringae*, *R. solanacearum* and in several other pathogens, type IV pili are found to be necessary for producing and attachment of biofilm, twitched motility, and pathogenic virulence (Nguyen et al. 2012; Kang et al. 2002).

During the plant infections, the formation as well as expression of flagella should be closely controlled for directed bacterial migration toward the apoplast and also prevent from being detected by PRRs (plasma membrane-localized pattern recognition receptors) which would then lead to initiation of pattern triggered immunity (PTI) (Macho and Zipfel 2014). The excess of flagellin monomers is known to be degraded by Apr A (alkaline protease A) (Pel et al. 2014).

4.1.5 Bacterial Invasion of Plant Tissue Mediated by Hijacking Stomatal Entry and Cell Wall Degeneration Enzymes

The plants as a part of their immune (innate) system keep their stomatal pores closed to inhibit ingression of bacteria (Melotto et al. 2006). But this defensive mechanism needs to be surpassed by phytopathogenic bacteria for gaining apoplastic access. It has been noted that Xcc (Gudesblat et al. 2009), *P. syringae* species (Melotto et al. 2006), and many other pathovars perturb stomatal immune system through secretion of phytotoxins. Virulent pathogens secrete varied molecules including toxins like syringolin and coronatine that enact as antistomate defense components (Melotto and Kunkel 2013) where they impede NRP1 (non-expresser of pathogenesis related 1) regulated SA (salicylic acid) signaling (Xin and He 2013). On the other hand, other pathogens secrete enzymes and specific proteins that degenerate the cell wall allowing them to enter plant tissues. Other literatures indicate another mechanism of overcoming phyto-defense systems through production of ice nucleating agents (INAs) which have been identified in *P. syringae* (Gaignard and Luisetti 1993), *X. campestris* (Gurian-Sherman and Lindow 1993), and *Pantoea ananatis* (Sauer et al. 2014). Water molecules are transformed by INAs into clathrin lattices identical to ice that elevate temperature allowing nucleation of ice with corresponding freezing of water at higher sub-zero temperatures (Garnham et al. 2011). Through this mechanism of ice-nucleation, the phytopathogens cause frost damage and thus gain access for entering into plants. Epiphytic bacteria also possess genes-rendering resistance to "freeze-thaw" that foster their survival irrespective of both environmental and biotic factors evoked frost conditions (Wu et al. 2012).

Additionally, phytopathogens also deploy certain secretion systems (mainly type II) through which wide arrays of enzymes are released (Korotkov et al. 2012). These contribute in degeneration of the structural molecules constituting cell walls of plants and also cause hydrolysis of the lamellae connecting individual plant cells which supply the pathogens with a source of carbon that promotes pathogens' propagation through apoplast and get distributed throughout the host plant tissues. *Xy. Fastidiosa* attributes in damaging the xylem's inter-vessel pit membranes in grapevine that facilitates pathogenic propagation (Sun et al. 2011). Extracellular enzymes like pectinases, proteases, xylanases, and cellulases are categorized as cell wall damaging enzymes that are critically related with *Xanthomonas spp*, Phytoplasma, and Xylella along with Erwinia and Pectobacterium genera (soft-rot pathogens) (Dejean et al. 2013; Lee et al. 2014; Toth et al. 2003).

4.1.6 Maneuvering Various Plant Protective Systems by Phytopathogenic Bacteria

The virulent microbes are also capable of synthesizing and secreting small phytotoxins that are responsible for potentiating bacterial virulency by suppressing host plant defensive mechanisms with subsequent enhancement of necrosis in tissues and chlorosis. While phytotoxins like syringopeptins and syringomycins directly deteriorate the plant cells, other toxins manipulate and interfere with different signaling pathways and metabolic activities that succor the invasion by the phytopathogens. *P. syringae* species synthesize toxins (modified peptides) such as mangotoxin, phaseolotoxin, and tabtoxin which trigger both tissue chlorosis as well as necrosis. The above-mentioned toxins primarily disrupt nitrogen metabolism by inhibiting the activity of targeted enzymes involved in biosynthesis of amino acids. The resultant nitrogen-rich intermediates are then successively utilized by the phytopathogens as a source of nutrition and food (Arrebola et al. 2011).

It has been observed that on release of hydrolysis-mediated toxic component of tabtoxin inside plant cell, glutamine synthetase is irreversibly inhibited and chlorophyll is degraded that consequently cause yellowing of tissues and chlorosis (Langston-Unkefer et al. 1987). On the other hand, another enzyme carbamoyl transferase is inhibited by Phaseolotoxin that also leads to similar consequences of host plant as an outcome of metabolic imbalance within plant cells (Bender et al. 1999).

The mechanisms of bacterial plant pathogens are not only restricted to these but are extensive in which they also disturb hormonal physiology in host plants and manipulate internal signal transduction cascades that exponentiate bacterial virulency and potentiate the pathogenic outcome. Structural as well as functional parallelism of most phytotoxic components with that of phytohormones like auxin has been observed. For example, coronatine which resembles the plant hormone Polyketide is involved in stimulating proliferation of apoplast, opening of stomata which finally confer to aggravated symptomatic development of phyto-diseases (Zeng and He 2010). The phyto-receptor complex COI1/JAZ (coronatine insensitive1/jasmonate ZIM-domain) senses coronatine that results in stimulation of JA (jasmonic acid) transduction in plants with simultaneous suppression of defense mechanisms arbitrated by SA (salicylic acid) signaling (Xin and He 2013).

Phytopathogens may also directly manipulate plant hormonal signaling pathways by encoding enzymes that are involved in synthesis of plant hormones. Several bacterial strains like *P. syringae*, *Ag. tumefaciens*, *Pantoea agglomerans*, and *Pseudomonas savastanoi* have been correlated with synthesis of abscisic acid (ABA), JA, indole acetic acid (auxin), cytokinins, and ethylene (Robert-Seilaniantz et al. 2011). The phytopathogens owing to their ability to produce or suppress various hormones directly exploit the critical crosstalk existing among the hormone transduction pathways that provide them the opportunity to subvert plant defensive mechanism and metabolism for their own benefit (Robert-Seilaniantz et al. 2011).

4.1.7 Effector Proteins-Mediated Bacterial Virulence

The phytopathogenic microorganisms are linked with secretion and release of miscellaneous virulent factors like phyto-toxins, enzymes, and other molecules for circumventing host plant defenses either directly into host plant's cytosolic environment or in the extracellular locale. *Xanthomonas* spp., *P. syringae*, and other hemi-biotrophic bacteria employ amalgamation of different secretory systems for effectively exporting and delivering secreted proteins called effectors responsible for maintaining structural and functional integrity of host plant's components to relevant locations to further potentiate the degree of infection. Co-ordinated secretory systems show prominent effect on the versatility of phytopathogens (Fig. 3a).

RsmA, in *P. aeruginosa*, functions as a molecular switch to coordinate between acute and chronic phases of infection causing translational suppression of T6SS, pel (pectate lyase), and psl mRNAs with corresponding upregulation in transcription of flagellar, T3SS, and T4SS genes (Moscoso et al. 2011). In Pss B728a, these T6SS and T3SS are negatively regulated by RetS and LadS (sensor kinases) (Records and Gross 2010). In Xanthomonas, previous reports indicate the regulatory role of QS over T2SS (Jha et al. 2005). Also, extensive researches are being conducted on modulation of hypersensitive response and pathogenicity (hrp) regulon which constitutes T3SS-related structural genes, T3SS regulators, and multiple T3ES (Buttner and Bonas 2010). During the infection phase, pathogenic bacteria keep tight control to deliver T3E hierarchically and temporally with the help of post-translational techniques (Galan et al. 2014). While *salmonella enterica* shows orderly recruitment and secretion of T3Es effectuated by chaperone-facilitated cytoplasmic cell sorting platform (Lara-Tejero et al. 2011), other bacterial pathogens deliver T3Es inside host cells by deploying chaperons, export control, and other hrp-associated (hpa) proteins (Lohou et al. 2013). Interaction between HpaB (global chaperone for T3E export) and HpaA in *R. solanacearum* causes selection of T3ES and guides them to HrcN (T3SS related ATPase) effectuating translocation (Buttner et al. 2006). Currently, the allosteric role of cdG in regulating HrcN action is also being explored that suggests its crosstalk with the dynamics of T3E translocation. In case of Pss B728a, regulated T3Es secretion is found to be essential during the phase of epiphytic growth which is marked by the prominent role of HopAA1 and HopZ3in promoting definitive leaf surface colonization (Lee et al. 2012).

Complex transportation mechanisms are required for translocating proteins and other molecules coordinately (Fig. 3a). Type I-VI transportation systems are engaged by gram-negative bacteria for delivering proteins into the extracellular milieu or inside the host cellular components (Gerlach and Hensel 2007). While T3SS plays a pivotal role in pathogenicity, T2SS is also widely used by different pathogens such as members of Ralstonia, Pseudomonas, Xanthomonas, and Erwinia genera for extracellular delivery of proteins (Jha et al. 2005; Johnson et al. 2006). T2ES mostly comprising of different virulence factors like cell-wall degeneration enzymes, toxins, and also proteases potentiate the virulency in plants. Gram-negative bacteria and members of Xanthomonas species are known to carry a lipA

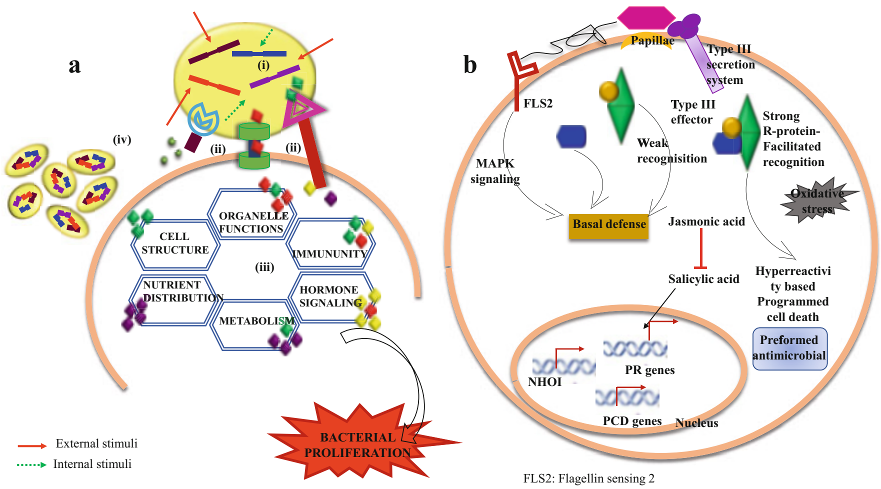

Fig. 3 (**a**) Bacterial effectors mediated mechanisms of phytopathogenesis: (1) extracellular and intracellular stimuli coordinated the expression of virulence genes (2) different secretion systems mediated effector translocation such as by type III secretion system (T3SS, T4SS, T2SS etc.), (3) Essential functions of host plants like immunity, metabolism, cellular structure, hormonal signals, distribution of nutrients etc, are all targeted and compromised by the effectors, (4) Host–pathogen interactions exponentially increases and diversifies virulent pathogenic gene families. (**b**) Phytopathogens targeted defense mechanism to promote disease development: Pathogenic avirulent factors upon strong recognition activate hyperreactivity (HR) dependent programmed cell death (PCD) which is a rapid response arresting the development of pathogenic infection. On the other hand, avirulent factors upon feeble recognition as well as flagellin or chitin through FLS2 also promotes basal defenses via different pathways including MAPK. Basal defenses subsequently stimulate expression of defense genes or induces late onset of pathogenic cell death. Formation of papillae at the site of nascent colonization of bacteria or site of fungal penetration corresponds to defense mechanism associated to cell wall. Jasmonic acid (JA) signaling pathway upon activation induces suppression of salicylic acid (SA) transduction pathway leading to repressed expression of specific pathogen related gene. Reactive oxygen species triggered oxidative stress is direct bactericidal in nature. Moreover, already existing antimicrobials help in repulsion of pathogenic activity. As a counter response to pathogen attack, signaling through programmed cell death facilitates cell death. The expression of the NHO1 gene expression triggered by nonhost and/or avirulent bacterial pathogens is necessary in certain cases of non-host resistance. *PR* pathogen related gene, *PCD* programmed cell death, *NHO1* non-host resistance 1

gene that encodes for a secreted lipase (type II) essential for imposing complete virulency by *X. oryzae pv. oryzae* (Aparna et al. 2009) and also *X. campestris pv. vesicatoria* (Tamir-Ariel et al. 2012). Additionally, it has seen discovered that T4SS which is generally associated with translocation of DNA and protein to the extracellular locale or inside host cells, mediates the transfer of T-DNA in *Ag. Tumefaciens* inside plant cells that confers in altered metabolic functions and morphology leading to tumor development (Bhatty et al. 2013; Gohlke and Deeken 2014).

These effectors improve microbial competence in the plant environment by interfering with essential phyto-processes. T3Es are reported to majorly suppress plant immune responses (Macho and Zipfel 2015). *Xanthomonas* and *Ralstonia* spp. members encode TAL effectors (transcription activator-like) which are phyto-transcription factors and are interlinked with promotion of plant virulence as well as providing a bacterial growth compatible environment (Bogdanove et al. 2010). *X. oryzae pv. oryzae* (rice pathogen) utilizes various TAL effectors to modify the gene expressions encoding sugar transporters (SWEET). The resulting sugar in apoplast, effluxed from the plant cells may be accompanied with release of water for maintenance of tissue osmotic balance that further alters the milieu of intracellular spaces thus providing advantage for bacterial infection (Streubel et al. 2013; Macho 2016). In *X. campestris*, AvrBs3 (TAL effector) upregulates UPA20 expression which regulates the size of plant cells and thereby causes enlargement of mesophyll cells leading to increased bacterial dissemination and growth (Kay et al. 2007). *P. syringae* associated T3ES like AvrPtoB, AvrRpt2, and HopX1 modulate the respective activities of ABA (Abscisic acid), auxin, and JA signal transducing pathways (Cui et al. 2013; Gimenez-Ibanez et al. 2014). Phyto-metabolic activities are also found to be directly modified by T3Es as they intrude secondary metabolites forming biosynthetic pathways. Perturbance of metabolism of phenylpropanoid by T3E belonging to the AvrF family secreted by *Pantoea stewartii* enhances the virulency of phytopathogens (Asselin et al. 2015). Similarly, mitochondrial activities are curbed by HopG1that impedes plant development and may also increase the virulency (Block et al. 2010).

4.1.8 Subduing Plant Defense Mechanisms by Phytopathogenic Bacteria

To circumvent the defense mechanisms of plants, pathogenic bacteria utilize diversified strategies to target and modulate core constituents of phyto-immunity including JA signal transducing pathway, HR (hypersensitive response)-dependent programmed cell death (PCD), defensive and basal gene expressions as well as cellular wall-related defense mechanisms. Table 2 and Fig. 3b represent certain host phyto-defenses that are commonly targeted by the virulent bacteria.

4.2 Viral Phyto-pathogenesis

Plant pathogenic viruses must expropriate host survival factors. The viral-encoded multifunctional proteins should strategically be involved in different phases of life cycle and elicit defensive responsiveness. Thus, most viral encoding protein usually performs the role of determinants of pathogens. The viral proteins regulating replication, encapsidation, transmission, and motility may play prominent role in directly or indirectly modulating pathogenesis.

Table 2 Few phytopathogen-mediated subversion of various plant defense mechanisms

Sr. No.	Phytopathogens	Particular defense targets	Probable mechanism to surpass the plant defense system
1	*P. syringae pv. tomato* DC3000	Various pathogenic DC3000 effectors like AvrPtoB, HopPtoD2, AvrPto, AvrRpt2 target hypersensitive response dependent programmed cell death, pathogenesis related gene expression, cellular wall mediated and basal defenses (Abramovitch et al. 2003; Espinosa et al. 2003; Bretz et al. 2003; Jamir et al. 2004; Hauck et al. 2003; Lim and Kunkel 2004)	Programmed cell death is restrained along with increased susceptibility toward infection. Often their functions are dependent on tyrosine phosphatase or cysteine protease enzymes activity. May also prevent formation of papillae while inducing alterations or downregulation of cell wall related and pathogenesis related genes expression. Basal defense mechanisms are attacked by targeting RIN4
		Effectors of type III secretion system (TTSS) target expression of non-host resistance (NHO1) gene or programmed cell death gene expression (Kang et al. 2003; Liang et al. 2003)	NHO1 resisting non-host pathogens is generally downregulated by coronatine insensitive 1 (COI1) dependent fashion. Moreover, the pathogen may also trigger expression of ACD5 (a ceramide kinase), which acts as a negatively regulates cell death
		Effectors of type III secretion system in association with coronatine toxin attack defense mechanisms controlled by jasmonic acid signal transduction pathway (He et al. 2004)	Activation of coronatine insensitive 1 (COI1) and Jasmonic acid insensitive 1 (JAI1) signaling pathways with simultaneous suppression of salicylic acid-based defense system
2	*X. campestris pv. vesicatoria*	Effectors of type III secretion system targets the cell wall associated defense system (Brown et al. 1995)	The virulent pathogens act by inhibiting papillae formation
3	*Rhizobium sp. NGR234*	The effector NopL targets expression of pathogen related genes (Bartsev et al. 2004)	The pathogen causes suppression of the pathogen related gene
4	*B. graminis f. sp. hordei*	Hypersensitive response dependent programmed cell death is targeted in addition to cell-wall mediated defense (Piffanelli et al. 2002)	Negative cell-death regulators MLO and BL1 genes are activated by the virulent pathogen that allows pathogenic invasion
5	*S. lycopersici*	The enzyme tomatinase targets already synthesized antimicrobials and hypersensitive reaction-based programmed cell death (Bouarab et al. 2002)	Tomatinase enzymes leads to degradation of saponins that provide plant defense. The degeneration of saponins results in formation of by products that contributes in repression of hypersensitive reaction-based programmed cell death
6	*P. infestans*	Soluble forms of glucans target hypersensitive reaction-based	

(continued)

Table 2 (continued)

Sr. No.	Phytopathogens	Particular defense targets	Probable mechanism to surpass the plant defense system
		plant defense mechanism and also generation of ROS (Doke 1975)	The ROS burst is inhibited with hypersensitive reaction suppression
7	*M. pinodes*	Suppression (Glycopeptide) targets pathogen related gene expression and hypersensitive reaction-based plant defense mechanism (Yoshioka et al. 1990)	plasma-membrane regulated ATPase activity is modulated to defense mechanism suppression

4.2.1 RNA-replicase-Associated Viral Proteins and Their Role in Phyto-pathogenicity

Viral RNA replicase (i.e., RNA dependent RNA polymerase) through modulation of viral replication process and consequent accumulation of virus, indirectly affects phyto-pathogenesis. Reports reveal that in both *Tobacco mosaic* (TMV) (Lewandowski and Dawson 1993; Chen et al. 1996) and *Pepper mild mottle* (PMMoV) (Yoon et al. 2006) viruses, mutation of p126/p183 proteins (RNA replicase-related proteins) resulted in truncated accumulation of virus along with attenuated symptoms. Similar observations were concluded in case of 2a protein mutation in *Cucumber mosaic* virus (CMV). The molecular mechanism of RNA replicase in development of the phyto-disease involves auxin (Aux) responsive pathway reprogramming. It is interconnected with TMV126/183K replicase crosstalk with IAA (indole acetic acid)/Aux that confers in corresponding enhancement in viral accumulation (Padmanabhan et al. 2008). RNA replicases function as elicitors of ETI (effector triggered immunity) operated by R-gene resulting in hypersensitive response. They may influence either localized lesions due to necrosis or systemic symptoms that are viral specific. These viral polymerases may also perform the role of breaking determinants of different resistance sources thereby modulating pathogenesis. It has been seen that *Tomato mosaic virus* replication proteins can subvert inhibitory interplay with resistance Tm-1 gene products via point mutation (Ishibashi et al. 2007). Alteration of single amino acid in methyltransferase domain of Potato virus X replicase assists disruption of JAX1 (jacalin-type lectin required for potexvirus resistance 1)-mediated resistance in *N. benthamiana* (transgenic) system (Sugawara et al. 2013).

4.2.2 Viral Coat Proteins-Mediated Pathogenicity

These are prototypical and multifunctional viral proteins that are associated with multifaceted functions such as encapsidation, replication, motility, translations, and even host defense responsive system (Ni and Cheng 2013). The expression of symptoms in concerned host plants is significantly affected when the coat proteins of respective CMV (Shintaku et al. 1992), TMV (Dawson and Bubrick 1988), Turnip crinkle virus (TCV) (Heaton et al. 1991), and Brome mosaic virus (Rao and Grantham 1996) undergo point mutations. The coat proteins of Tomato mosaic virus (TMV), CMV, Potato virus X(PVX), TCV, and PMMoV (Moffett 2009; Gilardi et al. 1998) act as avirulent factors eliciting resistance coordinated by the R gene (dominant). The coat proteins of TCV promote hypersensitive response development in resistant strain of Arabidopsis ecotype Dijon. The HRT and RRT host genes as well as SA signaling control such types of responses (Kachroo et al. 2000). The transcription factor TIP belonging to the NAC family interacts with coat proteins which stimulates the action of HRT gene and also inhibits TIP localization in nucleus (Ren et al. 2000, 2005). Photosystem II electron transport is prevented by tobamovirus-mediated infection which disrupts oxygen-evolving complex (OEC) (Rahoutei et al. 2000). Infected host plants revealed that the levels of OECPsbP and PsbQ (photosystem II proteins) are decreased in comparison to healthy plants. It has been recently demonstrated that while the interaction of PspB with Alfalfa mosaic virus's (AMV) coat protein results in inhibition of viral replication (Balasubramaniam et al. 2014), mutation of amino acid on the other hand renders virulence to the coat protein of CMV pepo strain that represses genes associated with chloroplast and photosynthesis thus causing chlorosis in tobacco plants infected with CMV (Mochizuki et al. 2014).

Similarly, interaction of coat protein of ToMV with IP-L (specific tobacco protein) causes localization of thylakoid membranes (Zhang et al. 2008). Also, the outer capsid P2 protein of phyto-reovirus upon interacting with the biosynthetic mediator of gibberellins known as entkaurene oxidase promotes dwarf symptoms (Zhu et al. 2005).

4.2.3 Viral Protein Interrelated with Movement and Their Role in Phyto-infections

The phyto-viruses are translocated into the cells of host plant with the help of movement proteins (Pallas et al. 2011; Lucas 2006) as these play an essential role in determining specificity of host (Mise et al. 1993). Various endogenous host factors are manipulated by the movement proteins facilitating the transportation of viral genome finally leading to alterations in physiology of plants with directly affecting the symptoms. The interaction of host plant factors with movement protein may facilitate or impede the viral movement as seen in case of the interplay between the crucial hydrogen peroxide decomposing enzyme tomato catalase (CAT) 1 and TGBp1 (triple gene block protein 1) of PepMV (Mathioudakis et al. 2013). This interaction leads to excessive peroxide scavenging and thus aid in development of PepMV infections by negatively regulating plant defense system. Movement protein also gives rise to hypersensitive reaction upon interaction with R gene. The avirulent determinant that potentiates Sw-5 (tomato gene)-induced resistance against tomato spotted wilt virus is suggested to be dependent on movement protein NSm (Peiro et al. 2014). The Potato virus X triple gene block protein 3 (TGBp3) promotes programmed cell death as well as unfolded protein response during the course of infections caused by PVX (Ye et al. 2013). The movement proteins also contribute in enhancing viral RNA silencing thus manipulating susceptibility of host plants mediated by stimulating silencing among cells (Amari et al. 2012).

4.2.4 Viral Suppressors of RNA Silencing

Certain viral proteins cause disruption of phyto-homeostasis counteracting with antiviral silencing and lead to development of disease symptomatology (Wang et al. 2012; Pallas and Garcıa 2011). Transgenic expression of RSSs (RNA silencing suppressors) leads to development of abnormalities that mimics disease symptoms (Chellappan et al. 2005; Dunoyer et al. 2004). These RSSs employ different mechanisms to interrupt the silencing processes, mainly at post transcriptional phase and sometimes also during transcription (Incarbone and Dunoyer 2013) that results in phyto-disease (Wang et al. 2012). miR167 upon being inactivated by RSSs like potyviral HCPro, tombusviral P19, and pecluviral P15 causes dysregulation of auxin response factor 8 which majorly contributes in development of abnormalities (Jay et al. 2011). It has also been suggested that inactivation of miRNAs regulating (negatively) NBS-LRR-R genes involved in autoimmune response induction by the RSSs may result in overexpression of these R genes conferring in lethal necrosis and other deleterious effect (Wang et al. 2012; Li et al. 2012; Shivaprasad et al. 2012). Similarly, the strategies of RSSs to inactivate AGO1 (Argonaute-1) and other effector proteins lead to inhibition of antiviral silencing and evoke developmental abnormalities as observed in cases of 2b and TGBp1proteins of CMV and PlAMV respectively (Zhang et al. 2006; Okano et al. 2014). Additionally, the ability of RSSs to induce pathogenic symptoms without blocking gene silencing directly has also been implied (Du et al. 2014). While the Cauliflower mosaic virus-associated RSS P6 interacts with ethylene signaling (Geri et al. 2004), CMV-related RSS 2b manipulates catalase of host plant (Inaba et al. 2011) and Potato virus A-associated HCPro RSS usurps microtubule-related protein (Haikonen et al. 2013). HCpro interactions are also responsible for precipitating proteasomal dysfunctions that contribute in pathogenicity (Pacheco et al. 2012). Performing the role of elicitors for ETI (effector triggered immunity), acting as second phyto-defensive layer, RSS can also cause developmental disease symptoms (Wang et al. 2012). For example, RSS P19 associated to tomato bushy stunt virus (TBSV) is known to induce hypersensitivity response (Chu et al. 2000).

4.2.5 Other Phytopathogenic Viral Factors

Together with the above-mentioned viral protein, certain addition proteins have also been researched that contribute to viral pathogenicity. P1 (Chiang et al. 2007), P3-6K1, CI (Desbiez et al. 2003), P3N-PIPO (Hisa et al. 2014), and 6K2 (Spetz and Valkonen 2004) proteins of potyviruses, p25 (Klein et al. 2007) and p31 (Rahim et al. 2007) of Beet necrotic yellow vein virus, are some of the examples of such viral determinants of pathogenicity. But the molecular mechanistic strategies of these proteins need to be thoroughly explored. Moreover, the nucleic acid of virus can also be function as direct determinants of viral pathogenicity. In case of defective interfering RNA (DI) of tombusvirus, DI-specific siRNA gets accumulated due to interference thereby saturating the capacity of silencing suppressor P19 to bind siRNA (Havelda et al. 2005).

4.3 Fungal Phyto-pathogenesis (Vadlapudi and Naidu 2011; Yang et al. 2017)

In case of fungal pathogenesis, well-conserved proteins are said to be used by fungal pathogens to induce infection. The fungal pathogens are known for deploying novel mechanisms to promote infections such as formation of appressoria, which are special infection structures that allow penetration of host plant cells.

The complete function of virulence protein is primarily facilitated by peroxisomes during this process of infection as in case of *Magnaporthe oryzae* (rice blast fungus). Colletotrichum higginsianum causes anthracnose disease in cruciferous plants via ChSTE7 gene that contributes in forming appressoria, vegetative and invasive growth in plant host tissue. Acetylation and other modes of histone modifications like methylation control regulation of transcription and structural chromatin organization to induce functional response. The genetic expression profiles are strategically transferred by the process of histone modification. The growth and fungal development are suggested to be controlled by SET-domain comprising proteins. It has been observed that Ash1like histone modification protein MoKMT2H essentially participates to induce pathogenesis of *M. oryzae*.

5 Conventional Strategic Approach for Phyto-infections and Disease Management

Epiphytotics (plants disease epidemics) transpires in crops every year and is a common phenomenon in different parts of the world. Plant pathogens negatively impact the both quality and quantity of the marketable agricultural yield that adversely affect the economy (Agrios 1997). Globally, phyto-diseases are responsible for 14% crop loss, while yield losses may account to 20–40% in the cultivates varieties (Baker et al. 1997). The pathogenic dissemination possesses a serious threat to the sustainable supply of food chain as it is responsible for enhancing the severity as well as the incidence of disease development (Savary et al. 2012). Although eradicating the phytopathogens completely still remains a challenge, extensive research is going on to explore new avenues for management of these infections in plants.

Among the various approaches that are associated in managing the plant infections, the conventional strategies include (1) implementing good and proper farming techniques that can resist infections, (2) destroying physically that is by plucking uprooting, etc. the affected or infected plant parts and tissues such as wilted roots, or stems, diseased fruits and other parts to hinder pathogen transmission from the infected to healthy parts, (3) control of pathogens through different measure which might involve insecticides or broad spectrum pesticides (e.g., copper) to check insect vectors, antibiotic to suppress infections precipitated by bacteria. These strategies mainly emphasize in preventing the plant disease to spread to healthy parts rather than on the cure of phyto-infections. Multi-integrated disease management practices are generally preferred. In cropping system and also in horticulture, use of disease-resistant plant and hybrid varieties is widely practiced. On the other hand, to minimize the use of hazardous and toxic chemical in environment, development of genetically modified plants is also being used that have the capacity of resisting development of pest and pathogens. However, such plants have limited cultivations due to their associated risk and low consumer acceptance (Hails 2000). Producers also take care and use sanitized and disinfected, certified virus/bacteria free tools and farming equipment to curb the growth of pathogens. Crop rotation techniques are followed and care is taken to prevent development of wound on plant surface that serves as an entry point for virulent pathogens. Additionally, bacteriophages are also used to control bacterial pathogenesis specifically to prevent bacterial infections. Phage-coded endolysins are also being attempted to be successfully incorporated in plants. As an alternative to use antimicrobial in agriculture, host-specific phages are being widely researched to reduce the environmental risks and concerns (Frampton et al. 2012). However, all these methods are associated with their individual shortcoming and thus require integrative approach of implementing two or more strategies to prevent crop loss to diseases. Although several countries witnessed evident abundancy in agricultural output as a consequence of green revolution (Pingali 2012), but this food and crop prosperity is gradually becoming disturbed due to pathogenic attack of food and plants, climatic changes, deterioration of soil quality, scarcity of arable lands, extensive increase in population, and many other associated factors.

In order to reinstate the food security, complementary strategies that are both efficacious and environmentally safe are need of the hour. In this context, the field of nanotechnology with its diversified applications and benefits may serve as an exciting opportunity to establish nano-weapons that may prove advantageous in phyto-disease management.

6 Nanotechnology and Its Impact on Agricultural Produce

For the past decades, extensive research on nanoscience and its associated technologies are constantly evolving in the fields of agriculture and also food system (Nair et al. 2010). Development of novel nanoparticles is being implemented to improve the chain of food supply with sustainable intensification and also by managing soil and water conditions. With at least one dimension having a size range of 1–100 nm, the nanomaterials are characterized by unique size-dependent properties, which include higher surface: volume ratio, better conductance ability, optical properties. Such varied features allow these nano-systems to be used not only to protect plants but also to provide them with nutrition (Ghormade et al. 2011). Nanomaterials are also being used for biotechnological purposes (Mukhopadhyay 2014; Dapkekar et al. 2018; Silva et al. 2010) which include amelioration of complications-associated soil structure providing stability against soil erosion and maintain salinity balance, increasing availability of nutrient and mobility, for identifying moisture content, availability of macronutrients, pH of soil, etc. and controlling environmental pollution, and finally as nano-cargoes for delivery of herbicides, pesticides, siRNAs, micronutrients, DNA, etc. The utilization of nanotechnology is not only restricted to the biotechnological advancements but is also extensively implemented in agriculture (Mohmood et al. 2013; Khiyami et al. 2014; Paknikar et al. 2005) where it is used for removing water or soil contamination, antimicrobial advanced food packing, nano-barcoding, biosensors, agro-commodities shelf life indicators, nanoparticles (clay-based)-mediated water management, bioremediation, etc. Figure 4 depicts the diversified application of nanotechnology in different fields of agriculture. For the past few decades, there has been steady increase in integrating nanotechnologies with agricultural practices. However, every avenue of

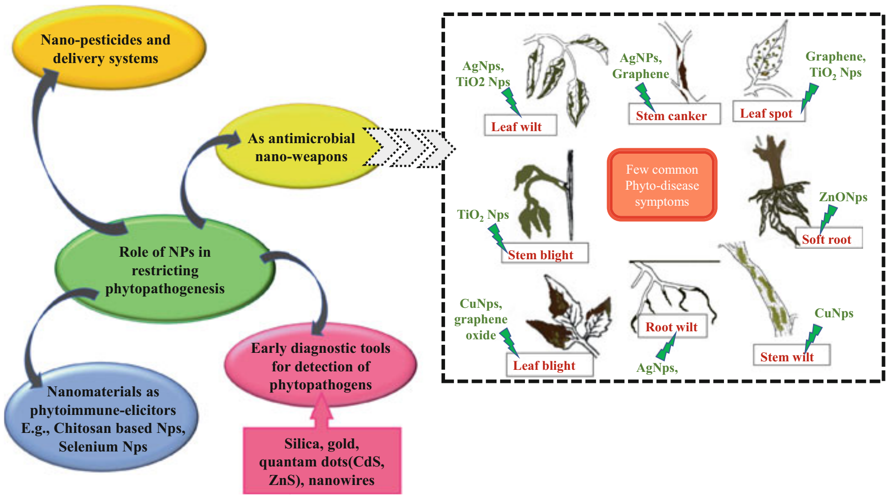

Fig. 4 Nanotechnology and their diversified role in management of plant diseases

nanotechnology and its advantages should be explored to the fullest and implemented strategically to maintain quality, sufficiency, and security of food supply, along with prevention of phyto-infections, diagnosis of plant disease, and genetic transformations.

7 Types of Nanoparticle and Their Role in Phytopathogen Suppression

7.1 Silver Nanoparticles (AgNps)

AgNps are well known for their broad spectrum and potent antibacterial activities and based on these properties, they were first investigated for management for phyto-diseases. Numerous studies have pointed out the efficacy in plant disease management. Prior application of nano-formulation containing silver and silica with a hydrophilic polymer (0.3 mg/L) on the cucumber leaves has been reported to show protective effect against *Podosphaera xanthii* (Park et al. 2006). Similarly, colloidal silver nano-formulation restricted the growth of *Sphaerotheca pannosa* and thus prevented the occurrence of rose powdery mildew (Kim et al. 2008). Similar studies were further substantiated with more detailed investigations in which silver nanoparticles (10–100 mg/L) were sprayed on cucumber and pumpkin leaves before and after the plants were infected with powdery mildew. The results indicated that at both stages of application, highest concentration of AgNps formulation was associated with only 20% disease incidence. Such results also indicated the rationale use of AgNps for rescue treatment as the nanoparticles produced comparable outcomes with that of a few commercially available fungicides (Lamsal et al. 2011a). Another study pointed out the efficacy of NanoAg formulation (100 mg/L) in suppressing anthracnose disease outbreak when applied to peppers prior to the infection (Lamsal et al. 2011b). It was also found that the postharvest disease severity in banana caused by *Colletotrichum musae* was significantly reduced when applied at a concentration of 2000 mg/L (Jagana et al. 2017). Silver nano-formulations are found to be effective in controlling various phytopathogens belonging to fungal and bacterial species like Xanthomonas, *Bacillus* sp., Acidovorax, Pseudomonas, and *Azotobacter* sp., (Fayaz et al. 2009; Krishnaraj et al. 2012; Mala et al. 2012). AgNps are also found to act synergistically with other Nps of Titanium dioxide (TiO_2), graphene oxide, silicon-aluminum carbide, and copper for providing protection against infections such as scabs, wilts, and molds caused to economically important agricultural crops like tomatoes, potatoes, and rice (Ocsoy et al. 2013; Boxi et al. 2016; Strayer et al. 2016; Aleksandrowicz-Trzcińska et al. 2018; Bhargava et al. 2018). Studies have pointed out AgNps stabilized by mucin derived from bovine submaxillary show potent action against seedling infections caused by both gram-negative and gram-positive bacteria such as Acidovorax, Xanthomonas, and Clavibacter, respectively (Makarovsky et al. 2018). On the other hand, bile salt sequestered AgNps were found to be effective against anthracnose disease (Shanmugam et al. 2015). While Ag-chitosan nanocomposites were found to prevent infections in strawberry caused by molds (Moussa et al. 2013), potent antifungal efficacy of amphopolycarboxyglycinate-stabilized silver nano-dispersions has been observed against phytopathogenic fungi like *Phytophthora infestans* isolated from pathogen infected potatoes (Krutyakov et al. 2016). AgNps are also being considered as alternative to pesticides owing to their wide range of antimicrobial potency.

7.2 Copper Nanoparticles (CuNps)

The crucial role of redox active transition element copper in plant biology is well accepted. This trace element is an integral component of most metalloenzymes that participate in different plant metabolic processes like photosynthesis respiration (Elmer and White 2018). Copper and its associated compounds comprised the first metal containing fungicides that were used to check pathogenic invasions and since then their wide-ranging antimicrobial activity has been utilized for antipathogenic management for centuries (Lamichhane et al. 2018). In order to resist bacterial blight copper hydroxide, Bordeaux mixture, copper oxychloride, etc. are still being used in pomegranate (Ruparelia et al. 2008). In the recent years, copper nanoparticles are being investigated for their anti-pathogenic activities and also being manufactured in large-scale industrial level. Various factors like of copper concentration, pH, temperature, and also pathogenic concentration affect the bioactivity of copper Nps (Ruparelia et al. 2008). Studies have pointed out CuNps treatment (0.2 mg/L) inhibited the growth of *X. axonopodis pv. punicae*, suppressing water-soaked lesion and thus protecting pomegranate leaves (Mondal and Mani 2012). On the other hand, CuNps formulation in conjugation with MBPF-01 (*Pseudomonas fluorescens* strain, antagonist strain of bacteria) conferred in 70% reduction in incidence of leaf blight infection in rice plants mediated by *X. oryzae pv. Oryzae* (Mondal et al. 2010). CuNps also manifest significant protective action against mungbean blight caused by *X. axonopodis pv. phaseoli* (Mondal and Mani 2012; Mondal et al. 2010) while wilt disease in tomato caused by Fusarium and Verticillium was markedly reduced on application of foliar nanoformulations of copper oxide, manganese oxide, and zinc oxide (Elmer and White 2016). Its destructive effects toward pathogens such as *Alternaria alternata*, Phoma, and *Curvularia lunata* are also well known (Kanhed et al. 2014). Recently, reports exhibited inhibitory efficacy of Cu-copper oxychloride (Cu-CoC) nano-formulation (50 mg/L) against *Phytophthora cinnamon.* Mycelial development as well as sporulation were suppressed by their synergistic effect when used against the phytopathogen *Alternaria alternata.* When used against *Pseudomonas syringae*, CuNps showed inhibitory action at 200 mg/L concentration. Studies have also pointed out the biocompatibility of these Nps as they do not adversely affect microorganisms beneficial for plants such as *Rhizobium* spp. and *Trichoderma harzianum* (Banik and Luque 2017). Novel nano-compounds such as fixed quaternary ammonium compounds, core shell copper composites, multivalent copper nanoparticles evaluated for their protective effects against tomato bacterial spot demonstrated bactericidal activity against causative agent *Xanthomonas perforans* (copper-resistant strain). Such copper nanoparticles have manifested evident control of phyto-diseases under greenhouse environmental conditions without negatively affecting the yield of tomatoes (Strayer-Scherer et al. 2018). They also efficiently inhibit *Phytophthora infestans* infections in tomatoes (Giannousi et al. 2013). When used against species belonging to fusarium genera, CuNps showed potent activity in resisting the phytopathogens *Fusarium equiseti*, *F. oxysporum*, *and F. culmorum* (Bramhanwade et al. 2016). Green synthesis of copper nanoparticles with leaf extract of papaya demonstrated significant inhibitory effect on soil-borne *Ralstonia solanacearum*, causing wilt under both normal and green house conditions (Chen et al. 2019). Additionally, CuO nanoparticles in the form foliar spray also showed bactericidal effect against *Fusarium oxysporum f. sp. niveum* in watermelons thereby preventing wilt. Under greenhouse surroundings also these nanoparticles evinced bactericidal actions with simultaneous increment in yield (Elmer and White 2018). Copper nano-formulations, synthesized using *Streptomyces zaomyceticus* Oc-5 and *Streptomyces pseudogriseolus* Acv-11, were found to be efficient antifungal activities against a number of phytopathogenic fungal strains *like Aspergillus niger*, *Pythium ultimum*, *Alternaria alternata*, *and Fusarium oxysporum* (Hassan et al. 2019).

7.3 Zinc Oxide (ZnO)-Based Nanoparticles

Inorganic zinc oxide possesses unique photocatalytic, optical, electrical as well as magnetic characteristics (Wang 2004). In addition to the wide-ranging usage in ceramics, pharmaceuticals, rubber industry, ZnO-Nps are also being extensively used in the agricultural industry. Apart from its function as micronutrient fertilizer, recent studies also document the antimicrobial efficacy of these Nps (Kołodziejczak-Radzimska and Jesionowski 2014; Dizaj et al. 2014). Zinkicide SG4 & 6 formulated as zinc oxide-based nano-formulations when tested against X. *citri subsp. citri* and *C. paradisi* exhibited potent bactericidal effect when applied in foliar spray and thus decreased the developmental incidence of citrus canker in sweet orange and prevented grape fruit (ruby red) rot (Graham et al. 2016). Zinkicide exhibited broad spectrum activities against disease caused by phytopathogenic fungi such as *Elsinoe fawcetti* and *Diaporthe citri*, lowering the incidence of citrus scab and melanose on grapefruit. The zinc oxide nanoparticles are also reported to resist the phytopathogenic effects of bacteria species like *Xanthomonas citri subsp. citri*, *E. coli*, and *X. alfalfa subsp. citrumelonis*. Moreover, their potential actions against *Botrytis cinerea* and *Penicillium expansum* causing postharvest disease are also documented. Conidiophores along with conidia development in *P. expansum* are restrained by the zinc-based nanoparticles that gradually lead to degeneration of the hyphae of pathogenic fungus thereby losing their ability to cause infection (He et al. 2011). In another studies ZnoNps when used in broth of mung bean broth and also in sand, resulted in significant repression of *F. graminearum* growth (Dimkpa et al. 2013a). It also inhibits the mycelial growth of pathogenic *Sclerotinia homoeocarpa* and thus prevents the appearance of dollar spots in cool season turfgrasses (Li et al. 2017). Nanocomposites of silica and zinc oxide were found to be toxic against *Cercospora beticola Sacc* and thus prevented sugar beet from the disease CLS (*Cercospora beticola Sacc*) (Derbalah et al. 2012). The inhibitory potency of these Nps against *Aspergillus fumigatus* and *A. flavus* has also been documented (Navale et al. 2015).

7.4 Titanium Dioxide (TiO_2) Nanoparticles

Owing to the chemical stability and nontoxic nature of titanium dioxide, their nano-formulations are widely being explored for environmental and agricultural applications. Having a long shelf life, TiO_2 has been reported to have antibacterial effect. It has been seen that titanium oxide Nps enhance the photosynthetic rate and promote growth of plants with simultaneous increment in yield and truncated disease severity (Chao and Choi 2005). In a field trial, titanium nanoparticle in the form of foliar spray manifested high protection against the phyto-diseases brown blotch as well as cercospora leaf spot in *Vigna unguiculata Walp* (Owolade et al. 2008). On the other hand, lesions in geranium plants and leaf spot disease in poinsettia plants caused by *Xanthomonas hortorum pv. pelargonii* and *Xanthomonas axonopodis pv. poinsettiicola* respectively were evidently reduced by the application of TiO_2 nano-formulations (Norman and Chen 2011). The TiO_2 nanoparticles are also known of imparting photocatalysis (Paret et al. 2013a). Studies have also revealed the potency of titanium hollow nanoparticles with or without silver doping as potent antifungal agents resisting the development of tomato or potato wilt caused by *Fusarium solani* and apple scab infection by *Venturia inaequalis*. Owing to the photocatalytic property, the significant antimicrobial efficacy was found in visible light. The titanium nano-formulations at low dose is also found to arrest the formation of fungal pathogenicity imparting naphthoquinone pigment in *Fusarium solani* (Boxi et al. 2016). When combined with zinc, the TiO2-Zn nanocomposites revealed reduction in severity bacterial spot in tomatoes with resisting the growth of *Xanthomonas perforans* without any adverse effect on the yield (Paret et al. 2013b). Colonization of *Hypocrea lixii circinelloides* and *Mucor circinelloides* is also significantly arrested by titanium oxide Nps thus preventing decay in wood (De Filpo et al. 2013). The oxidizing capability of titanium nanoparticles renders their antimicrobial efficacy. These Nps degrade the cellular membrane in bacteria leading to cellular components leakage that succumbs to impediments essential cellular activities (Frazer 2001). TiO_2 is often used as nanocarriers for silver nanoparticle that allows them not to get aggregated.

7.5 Other Nano-formulations Preventing Phyto-pathogenesis

In addition to all the nanoparticles discussed individually earlier, many of them are used in combination which may impart improved antimicrobial activities. Studies have indicated the potency of silver-silicon dioxide in preventing infections caused by *Phytophthora capsici*, *Fusarium oxysporum* as well as *Rhizoctonia solani* (pathogenic soyabean crop fungi) mediated by generation of reactive oxygen species in association with the released silver ions from the nanoparticles' surface. Such results imply promising role of Ag-SiO_2 nanocomposites in soyabean farming (Nguyen et al. 2016). The essential functions of sulfur in plant biology is well known and it is used as one of the primary components in many formulations used for commercially managing plant infections. Recently the efficacy of sulfur nanoparticles in organic farming is also being explored to protect crops and plants like apple, tomato grapes, and potatoes (Rao and Paria 2013). Sulfur nanoformulation (1000 mg/L) has been found to significantly reduce the invasion of *Erysiphe cichoracearum* in okra (Gogoi et al. 2013) and requires lower concentration than that of available commercial products to prevent the powdery mildew infection. While *Aspergillus niger* is efficiently restricted by sulfur Nps, early blight in tomatoes and apple-scab caused by *F. solani* and *V. inaequalis* is also decreased evidently by the small-sized nanoparticles (Rao and Paria 2013). As the nanoparticles deposit on the fungal cell wall, they contribute in its digestion leading to leakage of cytoplasmic components and subsequent fungicidal activity.

Other nanoparticles possessing antibacterial potency are the graphene oxide ones. The graphene oxide (GO) Nps have shown to inactivate *X. oryzae pv. oryzae* strain resistant to copper, *Aspergillus oryzae*, *A. niger*, *and F. oxysporum* (Chen et al. 2013). GONps demonstrated 90% cell death when applied against *Pseudomonas syringae*, *X. campestris pv. undulosa* and also are being used in treating macroconidia caused by *F. graminearum* and *oxysporum* (Chen et al. 2014). Thus, they can efficiently protect against various diseases like bacterial leaf blight and leaf streak, fungal head blight. Studies have also indicated silver graphene nanocomposites to show antipathogenic efficacy against *X. perforans* therefore reducing the incidence bacterial spot in tomato plant (Ocsoy et al. 2013). On the other hand, silver graphene composites containing dsDNA have prominent effect in reducing severity of phyto-disease as they accumulate on the pathogenic cells destroying them (Ocsoy et al. 2013). These nanocomposites in another study were found to show potent inhibitory action against both Cu-tolerant and sensitive *X. perforans* strain causing tomato bacterial spots (Strayer et al. 2016). Bactericidal activity was also observed against other pathogenic strains like *X. vesicatoria*, and *X. gardneri*. Another recent study has revealed the enhanced protective effect of GO-Ag nanoparticles against the rice pathogen *X. oryzae pv. oryzae* in comparison to silver nanoparticles alone (Liang et al. 2017). In floriculture, and specifically during the stages of growth as well as post-harvest, the fullerene nanoparticles can render protection against rose plants infection by resisting the growth of *B. cinerea* (Hao et al. 2017). Zinc oxide and magnesium oxide nanoparticles and also their combination nanocomposites (ZnO-MgO) and ZnO-$Mg(OH)_2$ are reported to possess potent bioactivity against the fungal phytopathogen *Colletotrichum gloeosporioides* responsible for causing anthracnose in economically important crops like *Persea americana* and *Carica papaya.* These nanoparticles cause structural degradation of conidia thereby preventing its germination and thus can prevent anthracnose disease commonly occurring in tropical fruits (De la Rosa-García et al. 2018). MgO nanoparticles when used for treating roots of tomato seedlings depicted efficacy in protecting them against the incidence of infection caused by *Ralstonia solanacearum* while another study revealed their efficacy in inhibiting the Cu-resistant strain of *X. perforan* (Imada et al. 2016; Liao et al. 2019).

7.6 Suppression of Phytopathogens by Green-synthesized Nanoparticles

In the recent years, researchers have concentrated in the field related to green synthesis and its rationale utilization to resist phytopathogens and their adverse effects. Ag, Cu, gold (Au), Zn, and other metallic nanoparticles formulated as biosynthetic preparations are known to exhibit broad spectrum antipathogenic activities with potent antibacterial efficacy against both gram-positive and -negative bacteria including *Bacillus subtilis*, *S. aureus*, and E. coli and also against certain virulent fungi like *Aspergillus niger*, *F. oxysporum* (Nisar et al. 2019). While green synthesized silver nanoparticles *using Streptomyces* exhibited strong antifungal activity against *A. niger*, *Alternaria alternata*, *Pythium ultimum*, *and F. oxysporum*, zinc oxide and titanium oxide nanoparticles formulated using extract of lemon fruit resisted the incidence of stem and root infection of sweet potato caused by *Dickeya dadantii* (Hossain et al. 2019). On the other hand, chamomile flower extract used as reducing agent in formulating magnesium oxide and manganese dioxide nanoparticles resisted the growth of *Acidovorax oryzae*, the bacterial strain responsible for brown stripe infection in rice.

8 The Nanoparticles and Their Mechanisms to Prevent Phytopathogenesis

8.1 Metallic Nanoparticles

The probable mechanisms of the metallic nanoparticles in imparting antipathogenic activity are documented in Table 3.

Table 3 Mechanism of antipathogenic action of few metallic nanoparticles

Sr. No.	Metallic nanoparticles	Probable mechanistic action
1	Silver nanoparticles (Lamsal et al. 2011a, b; Jo et al. 2009; Mishra et al. 2014)	Triggers contact inhibition against formation of pathogenic spores as well as fungal hyphae. Hyphal wall degradation in turn leads to suppression of conidial germination. The silver nanoparticles also prevent germination of spores and promote deposition in vascular bundles
2	Silver-chitosan nanocomposites (Moussa et al. 2013)	Contribute in lysing the pathogenic hyphae
3	Silver quenched hollow titanium dioxide nanoparticles (Boxi et al. 2016)	Stimulates the formation of disulfide bonds and bond between silver and sulfur with microbial cell-proteins leading to cell degeneration and the free radical burden causes cell death
4	Copper nanoparticles (Palza 2015; Hajipour et al. 2012)	Nanoparticles after entering the cells produce soluble ions contributing to "Trojan horse effect" and also disrupts bacterial cell membranes
5	Cupric oxide nanoparticles (Elmer and White 2018; Chen et al. 2019)	Stimulates the expression of pathogen-resistant 1 gene and polyphenol oxidase. As the nanoparticles are absorbed through the cytomembrane they induce nanomechanical damage to the microbial cells and also impede the activities motility and pathogenesis related genes
6	Magnesium oxide nanoparticles (Imada et al. 2016)	Superoxide radicals are generated by the nanoparticles in polyphenolic presence. Also upregulate the expression of salicylic acid governed pathogen related gene 1, jasmonic acid governed Lipoxygenase A, ethylene mediated Osm, and systemic resistance inducible GluA. These nano-formulations also cause b-1,3-glucanase as well as tyloses accumulation promoting systemic resistance. These Nps also ensure cell membrane damage and leakage of intracellular damage leading to cell death
7	Zinc nanoparticles (Jin et al. 2009)	The bacterial cell membrane is degraded by these Nps leading to leakage of intracellular components and subsequent cell death
8	Zinc oxide NPs (He et al. 2011; Dimkpa et al. 2013a; Gordon et al. 2011)	Triggers oxidative stress through formation of free radicals such as hydrogen peroxide causing cell damage. The released ions also promote acidification and damage to hyphae with restricted growth of conidiophores and conidia
9	Silver and zinc oxide nanocomposites (Li et al. 2017)	These nanocomposites upregulate stress response genes expressions, viz., glutathione S-transferase and superoxide dismutase 2 and also elevate the amount of nucleic acid in fungal hyphae. Zinc transporter (Shzrt1) are also overly expressed

(continued)

Table 3 (continued)

Sr. No.	Metallic nanoparticles	Probable mechanistic action
10	Graphene oxide nanoparticles (Chen et al. 2013, 2014; Liang et al. 2017)	As the nanoparticles directly interacts with bacterial cell, they mediate membrane disruption with consequent disturbance in membrane potential promoting lysis of the bacterial cells. On the other hand, sporic wall damage instigates leakage of intracellular components. Graphene oxide Nps mediated oxidative stress also plays a major role in their antipathogenic activity
11	Titanium dioxide nanoparticles (Linsebigler et al. 1995)	ROS mediated oxidative stress guide pathogenic cell wall and membrane degradation. They also oxidize organic matter and exhibit photocatalytic activity

8.2 Green Synthesized Biocompatible Nanoparticles

Although metallic Nps being formulated following green synthesis exhibit potent antipathogenic effect, however, the exact mechanism by which they exert their action is still not completely known. The Nps have been documented to disrupt the normal protein functions by either oxidizing cystine in the iron binding site or degrading iron–sulfur cluster or by exchanging catalytic or structural metals. They may also cater to depletion of cell membrane potential or membrane degradation leading to impairment in cell-membrane or functions cause oxidative stress through generation of ROS. The oxidant and antioxidant balance is disturbed as the Nps deplete antioxidants and also inhibit expression of iron (III) transporter gene thus interfering with uptake of nutrients. Moreover, the nanoparticles also precipitate genotoxicity. Some or all of these mechanisms function simultaneously and contribute in the antipathogenic action (Lemire et al. 2013). The positive or very low negative charge bearing nanoparticles adheres to the microbial membranes that are negatively charged through electrostatic attraction and disrupts the morphological components and structures. These alterations depolarize the membrane and interferes with permeability of cellular membrane as well as respiration that confers in cell structures degeneration and final cell death. The degeneration of cellular structure causes the exudation of DNA, proteins, enzymes, metabolites, and other internal contents. Additionally, irregular pits produced by nanoparticles on the cell wall of the pathogens allow them to penetrate into the periplasmic tissues and intracellular spaces of the microbial cells (Gahlawat and Choudhury 2019). AgNps formulated through green synthesis technique promoted rupturing of cell wall with subsequent release of cytoplasmic as well as nuclear constituents and cellular swelling which resulted into bacterial cell death of *Acidovorax oryzae* strain (RS-2) (Elbeshehy et al. 2015). Similarly, according to another report, on application of another biosynthesized silver nano-formulation against *Fusarium graminearum*, it distorted hyphae and degenerated cell wall inducing antifungal activity (Ibrahim et al. 2020).

Corresponding outcomes were also observed in case of application of such AgNps against various pathogenic microbes such as *A. alternata*, *Botrytis cinerea*, and *Trichosporon asahii* (Xia et al. 2016). The cytotoxicity of these Nps can also be imparted through the generation of oxidative stress mediated by accumulation of ROS (Vankar and Shukla 2012). As a consequence of the release of free radicals, microbial cell wall as well as other integral components such as DNA, proteins, and lipids are degraded. ROS may impart mutation of DNA, its deletion, double or single stranded breakage, protein crosslinking, etc. (Soenen et al. 2011) and all these have synergistic antibacterial effect.

8.3 Nanoparticles and Their Role as Immune Elicitors

The natural co-polymers, chitosan, and chitin are together available in nature. Chitosan being a biocompatible polymer has several advantages like lesser toxicity, and biodegradability and has been used as drug delivery system for years (Rodrigues et al. 2012). Studies have revealed immunomodulatory function of chitosan in plant systems. Chitosan Nps promote growth and protects plants and also have biocide actions (Sathiyabama and Parthasarathy 2016). Foliar application of chitosan Nps results in augmentation of innate immunity mediated by various mechanism such as enhancement of activities of defensive enzymes, upregulated expression of genes related to defense system, and increment in total phenolic content. Biocompatible chitosan Nps are also used as phytosanitary agents (Chandra et al. 2015). Reports have pointed out the antifungal potency of chitosan Nps to protect finger millet leaves from blast disease symptoms caused by the invasion of *Pyricularia grisea.* These nanoparticles trigger ROS formation and elevate peroxidase enzyme activity in the leaves thereby leading to the antifungal action (Sathiyabama and Manikandan 2016). Yet another study depicted the ability of chitosan Nps in evoking nitric oxide that induced innate defense activities and protected tea plants from symptoms of blister blight infection (Chandra et al. 2017). Chitosan nano-formulations were also found to exhibit protective effects against *F. oxysporum*, *P. capsici*, *X. campestris pv. vesicatoria*, and also *Erwinia carotovora* causing infections in tomatoes. When used in maize to protect it from Curvularia leaf spot disease, biocompatible copper-chitosan nanocomposites showed potent antimicrobial action and also promoted plant growth. These nanocomposites aggravated activities of antioxidant enzymes like superoxide dismutase, peroxidase, polyphenol oxidase, and phenylalanine ammonia-lyase thus inducing a defense response (Choudhary et al. 2017). Harpin is known for eliciting death of hypersensitive cells, incite plant to be disease as well as insect–resistant, and effectuate plant growth. Through activation of PAMP (pathogen-associated molecular pattern)-induced immunity, harpin renders plant disease-resistant. Despite such biological activities, its use as biopesticide is limited because of poor assimilation. To overcome this hurdle, chitosan is used as biocarrier of harpin and when harpinPss (an elicitor derived from *P. syringae pv. syringae*) incorporated chitosan Nps were used, they promoted peroxidase and phenylalanine ammonia lyase functions thereby resisting *Rhizoctonia solani* disease (Nadendla et al. 2018).

Selenium nanoparticles are also documented to produce resistance against root-knot nematode and thereby protect tomato plants from infection. Expression of PR-6 gene by selenium Nps results in upsurge of proteinase inhibitors activity and thus shields the roots and leaves from microbial invasion (Udalova et al. 2018). Similarly, when synthesized using *Trichoderma asperellum*, these selenium Nps restricted the incidence of downy mildew disease in pearl millets through truncated growth, viability of zoospore and sporulation of *Sclerospora graminicola* (Nandini et al. 2017). Moreover, selenium Nps are also found to arrest biofilm formation and viability of *Clavibacter michiganensis subsp. sepedonicus* (Perfileva et al. 2018).

9 Multifaceted Roles of Nanoparticles to Limit Plant–Pathogen Interactions

9.1 Nanomaterial-Based Diagnostic Tools for Phytopathogenic Detection

In order to efficiently manage plant disease, accurate and timely detection of the virulent pathogens with simultaneous applications of pesticides is of utmost importance. Nanoparticles may also be employed as biomarkers for detection of virulent phytopathogens (Chartuprayoon et al. 2013; Yao et al. 2009). They are either formulated for directly detecting the disease evoking pathogens or may sense certain conditions or signals that are associated with the phytopathogenic diseases. Nanochips comprise of oligoprobes (fluorescent) that are highly sensitive and specific in detection of even a single bacterial or viral nucleotide mutation. Various nanochips are being efficiently employed for pathogenic detection including antibodies conjugated silica (fluorescent) nanochips that can sense *Xanthomonas axonopodis pv. vesicatoria* (Yao et al. 2009) and gold nanoparticles acting as immunosensors for detecting *Tilletia indica*, the causative agent for karnal bunt disease in wheat (Singh et al. 2010). If utilized in certification of seed as well as in plant quarantine, these nano-sensors can provide an effective platform for detection of pathogenic diseases of plants. It is also known that stress conditions trigger various physiological changes in plants (Khan and Rizvi 2014). Stress-mediated stimulation of plant defense system coordinated majorly by salicylic and jasmonic acid and methyl jasmonate is one of such primary examples (Khan and Haque 2013). Copper (Cu) nanoparticles in combination with Au modified electrode is reported to be successfully used for identifying changes in level of ascorbic acid, salicylic acid, etc. in plants as well as seed which may help in detection of pathogen invasion (Wang et al. 2010). Advancements in such sensing technologies, which can identify alterations in physiological and/or biochemical parameters or directly monitor the pathogenic invasion may prove to be beneficial for management of phyto-diseases and protect economically important crops.

9.2 Nano-Pesticides and Efficient Carrier System

As nano-formulations act as efficient carrier systems allowing release of chemicals in controlled fashion, thus they can significantly reduce the quantity of pesticides that are generally required and its associated toxic outcome. The use of nano-pesticides will not only curb the conventional application rate of pesticides but will also exponentiate their effectivity owing to the timely and controlled release of chemicals as and when requires at the time of phyto-infection. The improved stability, lower viscosity, nanosize, and optical transparency confer nano-emulsions as better delivery cargoes for pesticides which may enhance the solubility of the active chemical ingredients and hence their bioavailability (Xu et al. 2010). Imidacloprid (1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine) formulated as controlled release nano-pesticides using PEG (polyethylene glycol) and other aliphatic diacids has shown significant potency in pest control for different crops (Adak et al. 2012). While polyhydroxyl alkanate is used as a biodegradable polymer to achieves sustainable release of pesticides (Pepperman et al. 1991), Intelimer, the thermosensitive polymer on the other hand controls pesticide release based on the temperature variations in different seasons which prevent undesired leaching. The suitability of different polymers like those from natural sources like proteins and polysaccharides, or polyacrylamide, and polystyrene categorized as synthetic polymers or even inorganic materials such as zeolites, glass beads, ceramics, etc. is being extensively researched for the production of nano-pesticides (Chuan et al. 2013). SDS (sodium dodecyl sulfate) fabricated silver-titanium dioxide nano-formulation of imidacloprid have shown improved protective efficacy against phytopathogen invasion in cabbages and cucumbers at seedling phase (Guan et al. 2010). On the other hand, studies have indicated encapsulation of zineb or mancozeb, the two common pesticides inside carbon nanotubes graft poly citric acid material helped in nano-fungicide formation which significantly arrested *A. alternata* mediated fungal spot development (Sarlak et al. 2014).

Thus, these nano-formulations, containing active pesticide chemical, increase the efficiency of protecting the crops and plants thereby escalating productivity of food with simultaneous reduction in adverse environmental impact (Chhipa 2017). Such nano-formulations also prevent unnecessary degradation of pesticides due to evaporation and leaching. And thus, with proper eco-toxicological screening they can be used as a promising technique for harnessing plant–pathogen interactions.

10 Nanotechnology and the Threats Imposed

10.1 Environmental Impact of Metallic Nanoparticles

Although the nanoparticles play major role in controlling the plant–pathogen interactions (Elmer and White 2018), but they also impose certain adverse effect on environment (Fig. 5). The nanoparticles which resist the growth of pathogenic microbes in the crops sometimes get dispersed in the surrounding soil, water bodies, and also atmosphere through probable processes like leaching, air current-mediated transfer, and through rainwater as well as transfer trophically (Gardea-Torresdey et al. 2014). It has been indicated that the microbes existing in the roots of plants, soil and sedimental deposits may also absorb these nanoparticles which finally undergo accumulation (Kim et al. 2016). Various organisms like mollusks, arthropods, protozoa, insects, fishes, and birds when consumes or utilize plant products, microbes or even the waste products assist in trophical transferring of the NPs from one level to another (De la Torre et al. 2015). Such process lays concern that the risk and adversities posed by the nanoparticles may be inherently passed to the offspring (Shimizu et al. 2009) which is evident among the marine ecosystem and organisms and also the food chain lining plants with herbivorous and carnivorous animals (De la Torre et al. 2015; Shimizu et al. 2009; Bielmyer-Fraser et al. 2014). Keeping such scenario in mind, the nanoparticle formulations application should be standardized and rationally used to maintain their safety and sustainability in agriculture. The probable risk associated with nanoparticles should be judged carefully and proper

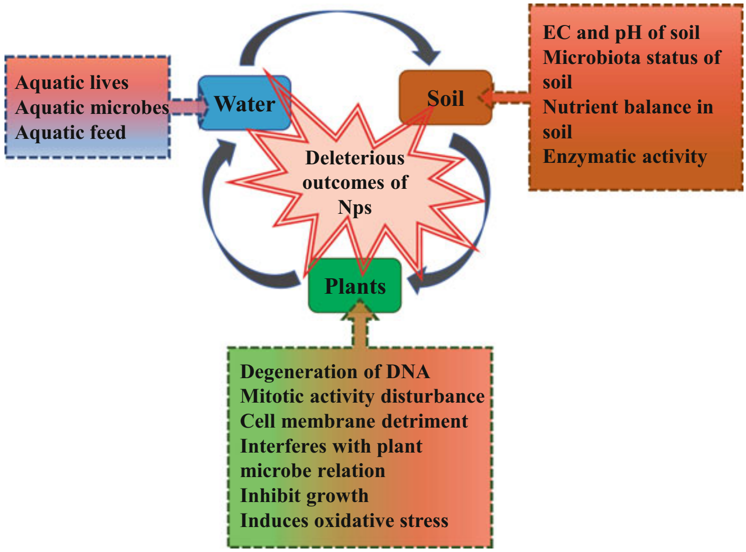

Fig. 5 Metallic nanoparticles and their negative impact on major components of agroecosystems like water soil and plants

knowledge about the nature of interaction of such Nps with the crops and plants along with the ecosystems in which they exist which includes other plants, animals and microbial organism is mandatory before they are being used in large scale field applications.

10.2 Toxic Impact of Nano-formulations on the Favorable Microbial Plant Interrelation

The epiphytic and endophytic association of various microbial organisms with the plants are well known as they exist in bulk soils surrounding rhizosphere and root. The microorganisms participate actively in producing auxins and phytohormones, N_2 fixation, solubilizing phosphate, etc. (Abdallah et al. 2019). Evaluation of respiratory activities as well enzymatic functions in soil allows understanding of the alterations occurring in microbial community in soil (Simonin and Richaume 2015). Reduction in biomass, truncated enzymatic actions of urease, dehydrogenase and phosphatase along with decreased levels of phospholipid (total) fatty acid are observed in the soil microbiota on application of copper oxide and titanium dioxide Nps in flooded field of rice (Xu et al. 2015). Saline and black soils also indicate similar alterations in enzymatic activities (catalase, invertase, etc.) and diversity of soil microbiota when nano-formulations of iron, cerium, zinc, etc. are applied (You et al. 2018). Application of cerium and zinc nanoparticles have exhibited to affect soil enzyme functionalities with reduction in thermogenic metabolic action, number of bacteria enabling phosphate and potassium solubilization, azotobacter, etc. (Chai et al. 2015). Similar reports are also presented for silver and zinc oxide Nps which interferes and diminishes the number of bacteria participating in nitrogen fixation like *Rhizobium leguminosarum Azotobacter chroococcum* solubilization of phosphates like *Arthrobacter sp.* MTCC 8160, *Serratia marcescens MTCC* 7642 and also formation biofilm like *Bacillus subtilis* MTCC 441, *Pseudomonas aeruginosa* MTCC 7763 (Chavan and Nadanathangam 2019). While silver Nps demonstrated bactericidal consequence and modified the soil bacterial population, the zinc nanoparticles were accompanied with bacteriostatic outcome (Chavan and Nadanathangam 2019). Studies have also indicated zinc nanocomposites to possess more toxicity than that of cerium nanoparticles (Bandyopadhyay et al. 2012) against the helpful soil microbiota.

10.3 Metallic Nanoparticles and Their Adverse Impact on Plants

The nanosize dimension of the particles allows acts as a dual sword in case of nano-formulations by facilitating the plants to fight against pathogens on one hand and on the other, adversely affecting beneficial microbes and surrounding plants, animals, fishes, birds, and even humans. The nano-formulations are applied to the plant parts present both above and below the ground and even on seedling stage. These nanoparticles may induce antipathogenic effects locally or undergo translocation all through the plant system and get accumulated in different plant parts thereby contributing to toxicity in different cells or organs (Kurepa et al. 2010). Exact size, surface of particles, and even composition determine the degree of Nps uptake and distribution along with other factors like concentration of nano-formulations and species on plant to which they are applied. As they get accumulated in different plant parts, the physiology of plant gets affected which in turn adversely effects plant growth. Minimal concentration of nanoparticles is reported to have high toxicities even with rare dispersal in environment (Ali and Ali 2019). Excessive nanoparticles when used in cultivation of crops like tomato, zucchini, and wheat disrupt electron transportation chain that subsequently cause oxidative stress. This impedes the processes involved in detoxifying free radicals and causes genotoxic outcome (Dimkpa et al. 2013b; Pakrashi et al. 2014) which in turn interferes with production of plant hormones and secondary metabolites essential for plant growth (Sanzari et al. 2019). The nano-formulation restrains transportation of water in plants, and promotes chromosomal disruption, reduction in growth hormone formation, disorders of metabolic system, alterations in profiles of gene transcription, etc. which makes the plants more susceptible to naturally occurring toxins like arsenic (Morales-Díaz and Ortega-Ortíz 2017).

11 Conclusion

Nanotechnology may serve as a magic bullet for developing multimodal techniques that will contribute to improving plant health either by disease monitoring or through controlling disease or strengthening the plant immune system. Various nanometallic formulation has shown to facilitate disease suppression at much lower concentrations than their counterpart fungicides or other pesticides. However, the associated limitation of such nano-formulation on adversely affecting plant health, soil microbiota, and beneficial soil microbial interactions with plants along with other toxicities imposed on environment and ecosystems should be strategically addressed. Integrating nanotechnology and plant pathology will mark the advent of new era of the use of functionalized metallic nanoparticles as pesticides, insecticides, nutrient fertilizers, etc. and would succor to conquer the impediments of food production globally.

Conflict of Interest The authors declare no conflict of interest.

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Zinc Oxide Nanoparticles Synthesis Using Herbal Plant Extracts and Its Applications

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1 Introduction

Agriculture, pharmacy, catalysis, medicine, textiles, consumer product manufacture and antimicrobial tests are just a few of the industries that use metal and metal oxide nanoparticles (NP) (Jay et al. 2016; Vaishali et al. 2018; Ginjupalli et al. 2018; Akintelu et al. 2019a, b). The uses of ZnO NPs in coatings, antimicrobial therapy, cosmetics, medicinal purposes, photocatalysis, insecticides, sunscreen materials, agriculture and antibacterial agent are particularly noteworthy (Jay et al. 2015; Devatha and Thalla 2018). Surgical tapes, antiseptic creams, shampoos and calamine lotions all contain ZnO NPs due to their exceptional antibacterial capabilities. ZnO NPs have been found to have a broad spectrum of antibacterial action at low doses (Chen et al. 2019). The US Food and Drug Administration has granted ZnO NPs a licence for their antibacterial and biosafety capabilities in medicinal applications (21, CFR 182, 8991). In this period, ZnO NPs are being used more frequently in electronics, rubber manufacturing, biosensors, transducers, pharmaceuticals and biomedical fields (Khatami et al. 2018). Researchers have universally accepted the synthesis of ZnO NPs utilising biosources as a reducing agent because of its eco-friendliness, nonhazardous reagents, simple to operate techniques, low energy consumption and cost-effectiveness (Khatami et al. 2018). Plant extracts' biological

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molecules and phytochemicals, like flavanones, alkaloids, tannins, saponins, polyphenols, and terpenoids, have been found to be responsible for the effective reduction in zinc precursors as compared to microbes (Amit et al. 2018). Plant-derived ZnO NPs offer superior antibacterial properties against human diseases and illnesses caused by bacteria and fungi (Asghari et al. 2016). Several plants have been described as good sources for the synthesis of nanoparticles, including *Cassia auriculata*, *Trifolium*, *Physalis alkekengi* L, *Justicia adhatoda*, *Trifolium pratense*, *Pongamia pinnata*, *Aloe Barbadensis*, *Plectranthus amboinicus*, *Limonia acidissima*, *Cochlospermum religiosum*, *Sedum alfredii* Hance, *Aspidopterys cordata* and *Bauhinia racemosa* (Król et al. 2017; Prashant et al. 2019; Chouke et al. 2020). The morphological identities of nanoparticles and ZnO NPs have been proven to influence their varied application in previous studies; ZnO NPs were characterised using UV visible spectroscopy, scanning tunnelling microscope, atomic force microscope, scanning electron microscope, dynamic light scattering, transmission electron microscope, differential scanning calorimetry, Fourier transmission infrared spectroscopy, energy dispersive X-ray and particle size analysis, to determine their varied characteristics (Iqbal et al. 2019). We present detailed scientific information on current advancements in the production and characterisation of ZnO NPs using plant materials in this study. Recent advances in the uses of phytosynthesised ZnO NPs were also discussed.

2 Different Methods Used in Nanoparticle Synthesis

2.1 Physical Method

Physical forces are employed to attract nanoscale particles in order to generate stable and well-defined nanoparticles in this technique. Examples include amorphous crystallisation, colloidal dispersion, physical fragmentation and vapour condensation (Krupa and Vimala 2016). Plasma technique, laser ablation and thermal evaporation are the most commonly utilised physical methods for ZnO NPs creation (Brintha and Ajitha 2015). Previous research has shown that laser ablation offers several distinct advantages, including the capacity to create ZnO NPs with a narrow shape, size and purity distribution (Ma et al. 2013). The efficiency and morphological identities of ZnO NPs generated by laser ablation are substantially determined by the laser's ablation period and wavelength (Manzoor et al. 2015). Another type of physical approach is thermal evaporation, in which powdered source materials are evaporated at high temperatures and the resulting vapour phase is condensed under high pressure to generate required ZnO NPs (Happy et al. 2017). This method has been used to make ZnO NPs in a variety of shapes, including nanorods, nanobelts, nanocombs and nanorings (Devatha and Thalla 2018). This method produces ZnO NPs with potential photocatalytic activity, making them suitable for degradation (Parita Basnet et al. 2018). Physical methods have a number of disadvantages, including the requirement for costly equipment, a large quantity of space for machine setup and high pressure and temperature (Chandrasekaran et al. 2016).

2.2 Chemical Methods

The most prevalent chemical methods for generating ZnO NPs are microemulsion, chemical reduction, precipitation, hydrothermal procedures and sol-gel (Brintha and Ajitha 2015). The sol-gel synthesis is the most widely used approach, which uses a chemical reagent and zinc precursor salt to control the pH of the solution and avoid $Zn(OH)_2$ precipitation. The solution is then thermally treated at high temperatures to produce ZnO NPs (Bekkari et al. 2017; Morandi et al. 2017). Stabilisers like as citrates or polyvinylpyrrolidone are commonly used throughout the synthesis process to control morphological characteristics and avoid ZnO NP aggregation (Naveed et al. 2017). The concentration of zinc precursor and other chemicals used during synthesis has been demonstrated to alter the shape and size of ZnO NPs generated. ZnO NPs with diameters ranging from nanometers to micrometres have been obtained by varying the concentration of zinc precursor and reagent (Naveed et al. 2017). The chemical process, on the other hand, has certain drawbacks because it requires a lot of energy, hazardous reagents and expensive equipment. According to the findings, remnants of a toxic reagent employed during synthesis can be found in manufactured nanoparticles, which could be dangerous and limit their applicability (Anshuman and Navendu 2014).

2.3 Green Methods

Biosynthesis of nanoparticles is a method of producing nanoparticles with biomedical uses utilising microbes and plants. This method is eco-friendly, cost-effective, biocompatible, safe and environmentally beneficial (Abdul et al. 2014). Plants, bacteria, fungi, algae and other organisms are all used in green synthesis. They enable large-scale manufacturing of ZnO NPs that are devoid of contaminants (Yuvakkumar et al. 2014). Biomimetic NPs have higher catalytic activity and need fewer expensive and harmful ingredients to produce. These wild strains and bio-extracts provide secondary metabolites that can be employed as reducers, stabilisers, or protective agents; for example, the synthesis of ZnO nanoflowers of uniform size from soluble proteins in *Bacillus licheniformis* cells shows increased photocatalytic activity and photostability, which are clearly manifested by the degradation of contaminating methylene blue (MB) dye in the presence of ZnO nanoflowers. The automatic degradation of MB is ineffective (observed by the control value) and through three repeated experimental cycles at different time intervals, it is found that 74% degradation clearly indicates the photostability of the produced ZnO nanoflowers (Auld 2001). The fungal strain *Aspergillus fumigatus*

TFR-8 has been used to synthesise oblate and hexagonal ZnO NPs ranging in size from 1.2 to 6.8 nm. These NPs are stable for 90 days, which are confirmed by measuring the hydrodynamic diameter of the NPs using a particle size analyser. These NPs only showed that the agglomeration formed 90 days later, indicating that NPs formed using fungal strain have high stability (Holmes et al. 2003). ZnO NPs with a size 36 nm synthesised from *Sargassum myriocystum* (macroalgae) obtained from Gulf of Mannar did not show significant changes even after 6 months, clearly demonstrating the stability of the NPs formed. The FTIR results confirmed that the soluble pigment fucoidan secreted by macroalgae is responsible for reducing and stabilising the nanoparticles (Table 1). Roots, leaves, stems, seeds and fruits have also been utilised to create NPs because their extract contains phytocompounds that act as a reducing and stabilising agent (Zong et al. 2014; Nachiyar et al. 2015; Ramesh et al. 2015; Xiao et al. 2016; Rajeshkumar 2016; Nagajyothi et al. 2013; Gnanajobitha et al. 2013). After 24, 48, 72, 96 and 120 h of NP creation, UV-Vis spectrophotometer results showed that ZnO NPs synthesised from *Trifolium pratense* flower extract had comparable peaks, indicating that the NPs generated were stable (Dobrucka and Długaszewska 2016). FTIR investigations indicated that the fruit extract of *Rosa canina* served as a reducing and stabilising agent for produced ZnO NPs. Carboxylic and phenolic acids found in fruit extract are responsible for bio-capping. *Aloe vera* leaf extract was used to make spherical ZnO NPs, with the free carboxylic and amino groups of the plant extract acting as both reducing and capping agents.

2.4 Nanoparticles of Zinc Oxide

ZnO is a semiconductor metal oxide with an n-type structure. Zinc oxide NP has gotten a lot of attention in the last couple of years because of its wide range of applications in electronics, optics and biological systems (Jamdagni et al. 2016; Anbuvannan et al. 2015a, b; Patil and Taranath 2016; Sundrarajan et al. 2015; Prasad and Jha 2009; Vanathi et al. 2014; Gunalan et al. 2012). Several types of inorganic metal oxides, such as TiO_2, CuO, and ZnO, have been produced and have remained in current investigations. ZnO NPs are the most interesting of these metal oxides since they are inexpensive to make, safe and simple to prepare (Jayaseelan et al. 2012). The US Food and Drug Administration has classed zinc oxide as a GRAS (generally recognised as safe) metal oxide (Pulit-prociak et al. 2016). Due to their wide bandwidth (3.37 eV) and high exciton binding energy (60 meV), ZnO NPs have incredible semiconductor capabilities, including strong catalytic activity, optical properties, UV filtering, and anti-inflammatory qualities, inflammation and healing (Mirzaei and Darroudi 2017; Patel et al. 2015; Stan et al. 2015; Sherly et al. 2014; Sangeetha et al. 2011; Elumalai and Velmurugan 2015; Sheikhloo et al. 2011). Because of its UV filtering properties, it has been widely used in cosmetics such as sunscreen (Wodka et al. 2010). Drug transport, anti-cancer, anti-diabetic, antibacterial, antifungal and agronomic qualities are only a few of the biological

Table 1 The relevance of zinc oxide nanoparticles generated from various plants and plant component extracts

S. No.	Plant (family)	Common name	Plant parts	Techniques for morphological assessment	Shape	Size	Reference
1	*Justicia adhatoda* (Acanthaceae)	Malabar nut	Leaf	SEM, XRD, FT-Raman, UV-Vis spectroscopy, and EDAX	Discoid	19–60 nm	Bhumi et al. (2014)
2	*Azadirachta indica* (Meliaceae)	Neem	Fresh Leaf	XRD	–	100–200 nm	Gnanasangeetha and Thambavani (2014)
3	*Coptidis Rhizoma* (Ranunculaceae)	Buchu	Dry leaves	TEM, HRTEM	Quasi-spherical agglomerates	15.8, 12–26	Thema et al. (2015)
4	*Aloe Vera* (Liliaceae)	Aloe Vera	Leaf extract	XRD	Spherical, oval, hexagonal	8–20	Ali et al. (2016)
5	*Agathosma betulina* (Rutaceae)	Buchu	Dry leaves	TEM, HRTEM	Quasi-spherical agglomerates	15.8, 12–26	Thema et al. (2015)
6	*Coptidis Rhizoma* (Ranunculaceae)	Coptis Rhizome	Dried Rhizome	TEM	Spherical, rod shaped	2.9–25.2	Nagajyothi et al. (2014)
7	*Phyllanthus niruri* (Phyllanthaceae)	Bhuiamla, stone breaker	Leaf extract	FE-SEM and XRD	Hexagonal wurtzite, quasi-spherical	25.61	Anbuvannan et al. (2015a, b)
8	*Pongamia pinnata* (Legumes)	Indian beech	Fresh leaves	XRD, DLS, SEM, TEM	Spherical, hexagonal, nano rod	26, Agglomeration of 100	Sundrarajan et al. (2015)
9	*Coriandrum sativum* (Apiaceae)	Coriander	Leaf extract	XRD, SEM, FTIR AND EDAX	Hexagonal	66 and 81	Gnanasangeetha and Thambavani (2013)
10	*Trifolium Pratense* (Legumes)	Red clover	Flower	XRD	Spherical	60–70	Dobrucka and Długaszewska (2016)
11	*Rosa canina* (Rosaceae)	Dog rose	Fruit extract	CH, MI), XRD, DLS	Spherical	11.3–243	Jafarirad et al. (2016)

(continued)

Table 1 (continued)

S. No.	Plant (family)	Common name	Plant parts	Techniques for morphological assessment	Shape	Size	Reference
12	*E. crassipes* (Pontederiaceae)	Water hyacinth	Leaf extract	SEM and TEM, XRD	Spherical without aggregation	32–36	Vanathi et al. (2014)
13	*Ocimum basilicum L. var. purpurascens* (Lamiaceae)	Red Rubin basil	Leaf extract	TEM, EDS, XRD	Hexagonal (wurtzite)	14.28–50	Abdul et al. (2014)
14	*Solanum nigrum* (Solanaceae)	Black nightshade	Leaf extract	XRD, FE-SEM and TEM	Wurtzite hexagonal, quasi-spherical	20–30 and 29.79	Ramesh et al. (2015)
15	*Aloe vera* (Liliaceae)	Aloe vera	Freeze dried leaf peel	SEM and TEM	Spherical, hexagonal	25–65	Qian et al. (2015)
16	*Anisochilus carnosus* (Lamiaceae)	Kapurli	Leaf extract	XRD, FE-SEM and TEM	Hexagonal wurtzite, quasi-spherical	20–56.14	Anbuvannan et al. (2015a, b)
17	*Azadirachta indica* (Meliaceae)	Neem	Leaf	TEM	Spherical	9.6–25.5	Bhuyan et al. (2015)
18	*Cocos nucifera* (Arecaceae)	Coconut	Coconut water	TEM, XRD	Spherical and predominantly hexagonal without any agglomeration	20–80	Krupa and Vimala (2016)
19	*Gossypium* (Malvaceae)	Cotton	Cellulosic fibre	XRD	Wurtzite, spherical, nano rod	13	Aladpoosh and Montazer (2015)
20	*Moringa oleifera* (Moringaceae)	Drumstick tree	Leaf	XRD, FE-SEM)	Spherical and granular nano sized shape with a group of aggregates	16–24	Elumalai et al. (2015)
21	*Azadirachta indica* (Meliaceae)	Neem	Fresh leaves	TEM, XRD	Hexagonal disk, nanobuds	10–30, 9–40	Madan et al. (2016)

22	*Parthenium hysterophorus L.* (Asteraceae)	Santa maria fever-few, carrot grass, congress weed	Leaf extract	XRD, TEM	Spherical, hexagonal	22–35 (50% plant extract), 75–90 (25% plant extract)	Rajiv et al. (2013)
23	*Plectranthus amboinicus* (Lamiaceae)	Mexican mint	Leaf extract	SEM	Rod shape nanoparticle with agglomerates	50–180	Fu and Fu (2015)
24	*Vitex negundo* (Lamiaceae)	Nochi	Leaf	SEM and EDX, XRD	Spherical	75–80, 38.17	Ambika and Sundrarajan (2015)
25	*Vitex negundo* (Lamiaceae)	Nochi	Flowers	XRD, DLS	Hexagonal	38.17, 10–130	Sundrarajan et al. (2015)
26	*S. album* (Santalaceae)	Sandalwood	Leaves	DLS and SEM, TEM	Nano rods	100, 70–140	Kavithaa et al. (2016)
27	*Nephelium lappaceum L.* (Sapindaceae)	Rambutan	Fruit peels	XRD	Needle-shaped forming agglomerate	50.95	Yuvakkumar et al. (2014)
28	*Calotropis Gigantea* (Apocynaceae)	Crown flower	Fresh leaves	SEM	Spherical shaped forming agglomerates	30–35	Vidya et al. (2013)
29	*Sphathodea campanulata* (Bignoniaceae)	African tulip tree	Leaf extract	TEM	Spherical	30–50	Ochieng et al. (2015)

applications (Sangani et al. 2015; Hameed et al. 2016; Movahedi et al. 2014; Martínková et al. 2009; Jain et al. 2014). Although ZnO is employed for targeted drug delivery, it still has a cytotoxicity problem that needs to be addressed (Ma et al. 2013). According to studies, ZnO NPs have a much stronger antibacterial impact than chemically generated ZnO NPs at extremely low concentrations of gram-negative and gram-positive bacteria (Vimala et al. 2014; Venkatachalam et al. 2016; Hazra et al. 2013). They've also been used in the production of rubber, paint, the removal of sulphur and arsenic from water, the features of protein adsorption and dental applications. Piezoelectric and pyroelectric capabilities are found in ZnO NPs (Jha 2007; Nagajyothi et al. 2014). They're employed to get rid of aquatic weeds that are resistant to all kinds of eradication methods, including physical, chemical and mechanical ones (Rajeshkumar 2016). Different morphologies of ZnO NPs have been documented, including nanoflake, nanoflower, nanobelt, nanorod and nanowire (Paulkumar et al. 2013, 2014; Rajeshkumar et al. 2014).

3 ZnO Nanoparticles Synthesis from Leaf Extracts

The synthesis and characterisation of ZnO nanoparticles generated by green and chemical techniques were carried out using *Coriandrum sativum* leaves. XRD, SEM, FTIR and EDAX were all used to characterise the ZnO NPs. In the green synthesis process, the average size was 66 nm, while in the chemical method, it was 81 nm. Biotechnology, sensors, medicinal, catalysis, optical devices, DNA labelling, medication delivery and water remediation were all expected to benefit from the ZnO nanoparticles made from *Coriandrum* leaf extract (Gnanasangeetha and Thambavani 2013).

The leaf extract of *Ocimum tenuiflorum* was used to synthesise zinc oxide nanoparticles. XRD, SEM and FTIR were used to characterise the prepared ZnO nanoparticles. The SEM picture revealed a hexagonal form with nanoparticles ranging in diameter from 11 to 25 nm (Raut et al. 2013). Zinc oxide nanoparticles were made using *Calotropis gigantea* leaf extract. SEM and XRD were used to examine the zinc nanoparticles that had been produced. The synthesised ZnO nanocrystals were on the order of 30–35 nm (Vidya et al. 2013), while the synthesis of *Calotropis procera* leaf extract was reported by Poovizhi and Krishnaveni and that FTIR and SEM were specific to the ZnO NPs synthesised. The size of the particles varies from 100 to 200 nm. Antibacterial activity against human and plant pathogenic bacteria has shown good sensitivity to green synthetic ZnO NPs at all concentrations.

Research indicated that *C. procera* ZnO nanoparticles have strong antibacterial activity against the tested human and plant bacterial pathogens as well as fungal diseases (Poovizhi and Krishnaveni 2015). To make zinc oxide nanoparticles, *Calotropis gigantea* leaf extract was employed. SEM and XRD were used to examine the produced zinc nanoparticles. (Ravindra et al. 2011).

The leaf extract of *Olea europaea* was used to synthesise zinc oxide nanoparticles. UV-Vis spectroscopy, FTIR, XRD and SEM were used to evaluate the produced ZnO nanoparticles. SEM examinations revealed that the average particle size was 500 nm and the thickness was about 20 nm. The presence of phytoconstituents such as amines, aldehydes, phenols and alcohols in aqueous *Olea europaea* leaf extract was shown by FTIR analysis, indicating that these were the surface-active molecules stabilising the zinc oxide nanosheets (Awwad et al. 2014). *Catharanthus roseus* chemotherapeutic compounds were renowned for their pain-relieving properties in cancer treatment. It is grown primarily for its alkaloids, which have anticancer properties (Jaleel et al. 2009). The leaf extract of *Catharanthus roseus* was used to make the zinc oxide nanoparticles. The generated zinc oxide nanoparticles were analysed using XRD, SEM, EDAX and FT-Raman spectroscopy. The particles were spherical in shape, with an average size of 23–57 nm, according to the SEM data. *Bacillus thuringiensis*, *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* were used to investigate the antibacterial activity of the ZnO-NPs generated. Antibacterial activity is highest in *Pseudomonas aeruginosa*, followed by *Staphylococcus aureus* (Bhumi and Savithramma 2014).

Zinc oxide nanoparticles were synthesised using *Adhatoda vasica* leaf extract. The synthesised ZnO NPs were analysed by UV-Vis spectroscopy, SEM, EDAX, XRD and FT-Raman spectroscopy. The discoid structure of synthesised ZnO NPs was discovered, with an average size of 19–60 nm. Phytochemicals discovered in the plant were blamed for the fast conversion of Zn+ ion to metallic zinc oxide nanoparticles. The generated ZnO NPs may limit bacterial cell proliferation in *Escherichia coli*, *Bacillus thuringiensis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. *Adhatoda vasica* is a good source for converting metallic zinc oxide into antimicrobial nanoparticles quickly. For the production of ZnO NPs, *Adhatoda vasica* was used as a reducing material as well as a surface stabilising agent (Bhumi et al. 2014).

A leaf extract from *Hibiscus rosa-sinensis* was used to make zinc oxide nanoparticles. The particle size and form of the generated nanoparticles were determined using SEM and XRD. The SEM image revealed nanoparticles with a spongy form and diameters ranging from 30 to 35 nm. Bala et al. demonstrated the generation of zinc oxide nanoparticles from *Hibiscus sabdariffa* leaf extract using UV-Vis spectroscopy, FTIR, XRD, HRTEM, EDX and FESEM. The antibacterial properties of the produced ZnO nanoparticles were tested on *Escherichia coli* and *Staphylococcus aureus* bacteria. Another study found that small-sized ZnO NPs stabilised by plant metabolites had a better anti-diabetic impact than large-sized ZnO particles in diabetic mice produced by streptozotocin (STZ) (Bala et al. 2015). *Hibiscus rosa-sinensis* blossoms are edible and are commonly used in salads in the Pacific Islands. In addition, the flower is utilised as a hair preparation (Devi and Gayathri 2014).

The leaf extracts of *Azadirachta indica* and *Emblica officinalis* were used to make zinc oxide nanoparticles. SEM, XRD, FTIR and EDAX were used to examine the shape, size, crystallinity and percentage content of the produced nanoparticles. SEM measurements revealed that the produced nanoparticles were in the 100–200 nm range. The presence of phytochemical elements such as alkaloids, carbohydrates, glycosides, steroids, flavonoids, terpenoids, tannins and steroids was discovered in the aqueous extracts of *Azadirachta indica* and *Emblica officinalis* leaf samples (Gnanasangeetha and Thambavani 2014). *Tanner's cassia* leaf extract was used to make the zinc oxide nanoparticles (*Cassia auriculata*). SEM, UV-Vis spectrophotometer and FTIR were used to confirm the produced zinc oxide nanoparticles. The generated ZnO NPs were found to be spherical in shape using SEM (Ramesh et al. 2014a).

Green tea leaf extract was used to make the zinc oxide nanoparticles *(Camellia sinensis*). XRD, UV-Vis spectrum and FTIR were used to analyse the produced zinc oxide nanoparticles. Senthilkumar and Sivakumar (2014) calculated the average size of the nanoparticles using XRD data to be 16 nm, but Shah et al. (2015) used UV-Vis spectroscopy, a particle size analyser and SEM to evaluate green tea and produced Zn nanoparticles. The size of the particles was evaluated using a particle size analyser, and they were discovered to be 853 nm in diameter. The antibacterial activity of the Zn nanoparticles generated was tested against gram-negative, gram-positive bacteria and a fungus. The study also showed that green produced Zn nanoparticles might be used as an alternative to antibacterial drugs currently on the market (Shah et al. 2015). In comparison to manufactured medicines, the antibacterial activity of synthesised ZnO NPs was superior and comparable (Senthilkumar and Sivakumar 2014).

Zinc oxide nanoparticles were synthesised using *Brassica oleracea* plant leaf extract. The UV-Vis spectrum and SEM were used to characterise the produced nanoparticles. The particles were round and rectangular in form. The diameters of produced nanoparticles in the solution were measured to be between 1 and 100 nm, according to the results. *Brassica oleraceae*'s entire plant body has aphrodisiac properties, and it played an important part in sustaining maleness. It was described as a revitalising plant in Siddha medicine, and it was known to contain coumarin, which was responsible for the hypolipidemic activity. Both gram-positive and gram-negative bacteria were resistant to the nanoparticles' antimicrobial action. As the concentration of zinc oxide nanoparticles grew, so did the antibacterial activity (Amrita et al. 2015).

Zinc oxide nanoparticles were synthesised using neem (*Azadirachta indicia*) plant leaf extract. FTIR spectroscopy and SEM analyses were used to analyse the produced ZnO nanoparticles. The particles were spindle-shaped and 50 μm in size, according to the SEM results (Noorjahan et al. 2015).

A leaf extract from *Pyrus pyrifolia* was used to make zinc oxide nanoparticles. The structural, morphological and optical properties of the generated nanoparticles were investigated using a UV-Vis spectrophotometer, XRD, FTIR AFM, and FE–SEM with EDX studies. The ZnO NPS that were synthesised were virtually spherical in form, with a particle size of roughly 45 nm. The photocatalytic investigation found that bio-ZnO NPs have the ability to colour breakdown methylene blue when exposed to sunlight. As a result, the research could be useful in water treatment plants and the textile industry (Parthiban and Sundaramurthy 2015).

Biological and chemical reducing agents were used to synthesise zinc oxide nanoparticles. *Pithecellobium dulce* and *Lagenaria siceraria* leaf extracts were utilised as reducing agents in the biological technique, while sodium hydroxide was used in the chemical method. The leaves of *P. dulce* were used in traditional medicine to cure earaches, leprosy, peptic ulcers, toothaches and venereal disorders, as well as having emollient, anodyne, larvicidic (Sugumaran et al. 2008), abortifacient and antidiabetic qualities. The leaf was employed as an astringent, the seed oil as spermicidal, anti-inflammatory, and anti-oedemia, the fruit and seed as edible and the bark as tannin (Mohammed et al. 2004). *Lagenaria siceraria* was utilised as a food because of its diuretic and anti-swelling properties (Wang and Ng 2000). Anasarca, ascites and beriberi were treated using a decoction of *Lagenaria siceraria* (Anandh et al. 2014). In comparison to manufactured pharmaceuticals, biologically generated ZnO nanoparticles showed greater antibacterial activity than chemically synthesised ZnO nanoparticles (Prakash and Kalyanasundharam 2015).

The leaf extract of *Thevetia peruviana* was used to synthesise zinc nanoparticles. The plant contained thevetin, a deadly toxin that was utilised as a cardiac stimulant (Singh et al. 2012). These plant poisons were also utilised to fight biological pests (Kareru et al. 2010). UV-visible spectroscopy, FTIR, Particle Size Analyser, XRD, SEM, TEM and inductively coupled plasma-optical emission spectrophotometer were used to characterise the zinc oxide nanoparticles that were manufactured. The average particle size of synthesised zinc nanoparticles is 53 nanometers. SEM and TEM measurements revealed the presence of triangular shaped and polydispersed zinc nanoparticles with a grain size of 50 ± 5 nm. The generated Zinc nanoparticles were applied to *Arachis hypogaea* L (peanut) pot-culture to test soil microbial population, soil exo-enzyme activities and physiological growth parameters of peanut plants. In comparison to the control, zinc nanoparticles applied to peanut pot-culture exhibited significant variations in soil microbial and enzyme activity and increased the physiological growth indices of peanut plants (Sindhura et al. 2015).

The zinc oxide nanoparticles were made with *Aloe vera* leaf extract. XRD, SEM, UV-Vis spectroscopy, PL, BET and TGA were used to characterise the generated ZnO nanoparticles. The particles were hexagonal in form and averaged 22.18 nm in size. The nanoparticles' photodegradation and antibacterial activity were investigated. Synthesized nanoparticles were found to be sensitive to both gram-positive and gram-negative bacteria in antibacterial tests (Varghese and George 2015).

Corymbia citriodora leaf extract was used to make zinc oxide nanoparticles. SEM, EDX, XRD, UV-is spectroscopy, Raman spectroscopy and TGA were used to characterise the biosynthesised ZnO NPs. With an average size of 64 nm, the produced nanoparticles had a polyhedron form and a size range of 20–120 nm. They also demonstrated exceptional dispersibility. Methylene blue photodegradation was used to test the photocatalytic activity of biosynthesised ZnO NPs. Because of their smaller size, biosynthesised ZnO NPs displayed better photocatalytic performance than typical hydrothermally generated ZnO NPs (Zheng et al. 2015) (Table 1).

4 ZnO Nanoparticles Synthesis from Stem and Root Extracts

Zinc oxide nanoparticles were made from the stem extract of *Euphorbia tirucalli*. XRD and SEM were used to examine the particle size, topography and morphology of the produced ZnO nanoparticles. The particles were spherical in shape and agglomerates of nanocrystallites with a diameter of 20 nm. The branches (stems) of *Euphorbia tirucalli* were used as capping and reducing agents in the production of ZnO nanoparticles (Hiremath et al. 2013).

Zinc oxide nanoparticles were synthesised using a stem extract of *Ruta graveolens*. PXRD, UV-visible spectroscopy, SEM and TEM were used to examine the formation of ZnO nanoparticles. According to SEM measurements, the particles were spherical in shape with an average crystallite size of 28 nm. *Ruta graveolens* included a chemical used in herbal veterinary medicine. ZnO nanoparticles were found to be effective at inhibiting the antioxidant mechanism of 1,1-diphenyl-2-picrylhydrazyl free radicals. Gram-negative bacterial species such as *Klebsiella aerogenes*, *Pseudomonas aeruginosa*, *Escherichia coli*, and gram-positive *Staphylococcus aureus* ((Lingaraju et al. 2015) showed considerable bactericidal action against ZnO NPs.

Tinospora cordifolia stem extract was used to make zinc oxide nanoparticles using a biological approach. SEM, EDX and FTIR were used to characterise the produced zinc oxide nanoparticles. SEM measurements revealed that the average size of ZnO nanoparticles is 37 nm, with a spherical form. The presence of zinc and oxygen in the produced ZnO nanoparticles was confirmed by EDX data. The presence of reducing and capping biomolecules that were responsible for the formation of ZnO nanoparticles was clearly demonstrated by FTIR investigations (Raj and Jayalaksmy 2015b). *Tinospora cordifolia* included bioactive components such as alkaloids, phenolics and steroids including tiospirone, tinosporide, columbine and others, which were responsible for its therapeutic properties (Pandey et al. 2012; Shanthi and Nelson 2013).

Boswellia ovalifoliolata stem bark extract was used to make zinc oxide nanoparticles. The generated zinc oxide nanoparticles were analysed using UV-visible spectroscopy, XRD, FTIR, DLS, TEM and Zeta potential. The zeta potential was used to determine the particle size, which was found to be 20.3 nm. The disc diffusion method was used to test *Boswellia* Zn NPs in vitro against hazardous fungus and bacteria isolated from biofilms generated in drinking water PVC pipelines. When compared to antifungal activity, *Boswellia* Zn NPs demonstrated good antibacterial action (Supraja et al. 2015).

Zinc oxide nanoparticles were made using the root extract of *Zingiber officinale*. SEM, EDX and FTIR were used to characterise the produced zinc oxide nanoparticles. The nanoparticles were determined to be 30–50 nm in size and spherical in form (Raj and Jayalaksmy 2015a). Gingerols, shogaols, zingerone, paradol, terpineol, terpenes, borneol, geraniol, limonene, linalool, alpha zingiberene and other flavonoids and polyphenolic substances were abundant in ginger (Ghosh et al. 2011) (Table 1).

5 ZnO Nanoparticles Synthesis from Peel, Flower, Fruit and Latex Extracts

Zinc oxide nanoparticles were synthesised using *Citrus aurantifolia* fruits. SEM, UV-Vis spectrophotometer and FTIR were used to investigate the morphology, structure and stability of the produced ZnO nanoparticles. The particles were spherical in form and ranged in dimension from 9 to 10 nm. Phytoconstituents such as alcohols, aldehydes and amines were discovered in *Citrus aurantifolia* extract (Ramesh et al. 2014b).

Citrus aurantifolia fruit extract was used to make zinc oxide nanoparticles. FE-SEM, XRD and PL spectroscopy were used to analyse the produced zinc oxide nanoparticles. FESEM imaging revealed the production of spherical nanoparticles with a size range of 50–200 nm. The synthesis of zinc oxide nanoparticles using citrus extracts was found to be comparable to that obtained using traditional reduction methods such as hexamethylenetetramine or cetyltrimethylammonium bromide, suggesting that it could be a good alternative for synthesis of ZnO nanoparticles using biomaterials (Samat and Nor 2012).

Emblica officinalis fruit extract was used to make zinc oxide nanoparticles. *Staphylococcus epidermidis*, *Klebsiella pneumonia*, *Bacillus subtilis*, *Streptococcus pneumonia*, *Escherichia coli*, and *Salmonella typhi* were examined for antibiotic action, as were two fungus pathogens, *Aspergillus niger* and *Candida albicans.* According to the findings, green generated zinc oxide nanoparticles derived from *E. officinalis* could be used as an antibacterial agent in traditional medicine (Anbukkarasi et al. 2015).

Grapefruit (*Citrus paradisi*) peel extract has been discovered to be useful in the production of zinc oxide nanoparticles. The structural, morphological and optical features of the nanoparticles were characterised using a TEM, UV-Vis spectrophotometer, FTIR and DLS studies. The nanoparticles were spherical shape and measured 12–72 nm in diameter. The research showed a green way to make ZnO nanoparticles with strong photocatalytic and antioxidant activities. The generated ZnO NPs were extremely stable, degrading methylene blue by more than 56% after 6.0 h in the sun. Furthermore, the study established that ZnO NPs were responsible for substantial antioxidant activity ($\geq$80% for 1.2 mM) (Krupa and Vimala 2016).

Punica granatum peel extract was used in the green production of zinc oxide nanoparticles. UV-visible spectroscopy and SEM were used to characterise the produced zinc oxide nanoparticles. The particles had a diameter of 50–100 nm and were round and square in form (Mishra and Sharma 2015).

Zinc oxide nanoparticles were synthesised using *Trifolium pratense* flower extract. UV-visible spectroscopy, XRD, FTIR, SEM and EDX were used to characterise the produced Zinc Oxide nanoparticles. The produced ZnO nanoparticles were agglomerated into particles ranging in size from less than 100 to 190 nm. The antibacterial activity of ZnO nanoparticles made from *T. pratense* flower extract was found to be effective against all strains tested (Dobrucka and Dugaszewska 2015).

The milky latex extract of *Calotropis procera* was used to make the zinc oxide nanoparticles. XRD, TEM, SEM and UV-Vis spectroscopy were used to analyse the produced zinc oxide nanoparticles. The morphology of ZnO NPs contained in *Calotropis* matrix showed negligible agglomeration and particle sizes of about 5 nm across the carbon coated copper grid, with an average particle size of 5 to 40 nm. Photoluminescence (PL) experiments were carried out to highlight the emission features of ZnO NPs (Ravindra et al. 2011) (Table 1).

6 ZnO Nanoparticles Synthesis from Whole Plant Extracts

Zinc oxide nanoparticles were made using aqueous extracts of mature leaves, stems, roots, fresh and dried stem bark, immature and ripened fruits and petals of *Morinda pubescens*. The UV-visible spectroscopic technique was used to characterise zinc oxide nanoparticles. The UV-Vis absorbance peak of the nanoparticle suspension was between 290 and 300 nm (Shekhawat and Manokari 2014).

The aqueous extracts of leaves, stems and roots of *Hybanthus enneaspermus* (L.) F. Muell were used to make zinc oxide (ZnO) nanoparticles. The produced ZnO nanoparticles were analysed using UV-Vis spectrophotometry (Shekhawat and Manokari 2014). Anti-inflammatory, antitussive, antiplasmodial, anticonvulsant, antibacterial, anti-oxidant, antifungal, hypolipidemic and free radical scavenging properties have been described for the ethnobotanical herb *Hybanthus enneaspermus* (Boominathan et al. 2004; Sahoo et al. 2006; Satheesh and Kottai 2012; Patel et al. 2011; Arumugam et al. 2011).

The production of zinc oxide nanoparticles from *Hemidesmus indicus* leaves, stem and root extracts has been described. Aqueous extracts of leaves, stems and roots included a variety of primary and secondary compounds involved in nanoparticle creation. The zinc oxide nanoparticles were analysed using a UV-visible spectrophotometer, with absorption peaks between 29 and 310 nm, proving the creation of zinc oxide nanoparticles in the reaction mixture (Manokari and Shekhawat 2015).

Zinc oxide nanoparticles were made using aqueous extracts of *Ficus benghalensis* stems, leaves, aerial roots, roots, fruits and fresh and dried stem bark extracts. The UV-visible spectroscopic technique was used to characterise zinc nanoparticles. The greatest UV-Vis absorbance peak in the nanoparticle dispersion was between 290 nm and 300 nm, indicating the production of zinc oxide nanoparticles. The whole plant (*Ficus benghalensis*) was used in traditional Indian medicine to treat ulcers, leprosy, syphilis, diabetes, biliousness, diarrhoea, skin illnesses, inflammation and other ailments. Its milky latex was said to have sexual qualities (Shekhawat et al. 2015a).

Henna (*Lawsonia inermis* L.) plant extracts were used in the biological production of zinc oxide nanoparticles. Colour shifts from brown to pale green validated the produced nanoparticles, which were then analysed using a UV-visible spectrophotometer. Absorption peaks in the region of 296 nm to 302 nm confirmed the existence of zinc oxide nanoparticles in the solution. *Henna* is a traditional product with religious ties that has been used for medical and cosmetic purposes for millennia. (Shekhawat et al. 2015b).

The aqueous extracts of the leaves, stem, roots and fruits of *Micrococca mercurialis* (L.) Benth were used to make zinc oxide (ZnO) nanoparticles. A UV-visible spectrophotometer was used to characterise and validate the manufactured ZnO nanoparticles. UV absorbance peaks were observed at 305 nm, 299 nm, 311 nm and 302 nm in the reaction mixtures. The plant (*Micrococca mercurialis*) was discovered to be high in primary and secondary metabolites such as proteins, steroids and alkaloids, all of which contributed to the biogenic synthesis of ZnO nanoparticles (Manokari et al. 2016b). Purgative and anticancer properties have been found for this plant (Jeyachandran and Bastin 2013).

To create zinc oxide (ZnO) nanoparticles, researchers employed aqueous extracts of *Couroupita guianensis* Aubl. leaves, stem, flower petals and bark. For the characterisation and validation of the produced ZnO nanoparticles, UV-visible spectral measurements were done, with the absorbance peak recorded in the range of 290–302 nm (Manokari and Shekhawat 2016). The entire plant is used to treat colds, stomachaches, toothaches, throat infections, tumours and other ailments (Biset et al. 2009; Pradhan et al. 2009).

Zinc oxide (ZnO) nanoparticles were made using aqueous extracts of *Melia azedarach* L. stems, roots, flowers, leaves and fruits. UV-visible spectral measurements were taken to characterise and validate the generated ZnO nanoparticles, with the absorbance peak reported in the 290–330 nm range. *Melia azedarach* is high in alkaloids, glycosides, sterols, tannins, phenolic compounds, saponins, flavonoids and other physiologically active phytocompounds (Manokari et al. 2016a).

Due to its diverse biological activity, *Duranta erecta* has achieved horticultural and medicinal relevance (Ravindran et al. 2016). Against human diseases, this plant also has antioxidant, antibacterial and antimicrobial properties (Bangou et al. 2012; Prabhakar et al. 2015). The production of zinc oxide nanoparticles was reported utilising aqueous extracts of *Duranta erecta* L. leaves, stem, root, flowers and fruit extract. UV-Vis spectrophotometric analysis was used to analyse the produced ZnO nanoparticles. At 302 nm, the leaf extract displayed a substantial absorbance peak, while the stem and flower peaks were at 299 nm, the roots were at 293 nm, and the fruit extract solution peak was at 317 nm. The study determined the usefulness of *D. erecta* in the nano-field, which might be of significant interest in the development of novel pharmaceuticals in the medical sector, as well as the manufacturing of pesticides and nano-biofertilisers in agriculture revolutionisation (Ravindran et al. 2016) (Table 1).

7 Applications

7.1 ZnO NPs in Agriculture

The widespread use of commercially accessible antibiotics in the treatment of farm animals has resulted in the emergence of multidrug-resistant bacterial and fungal species (Sirelkhatim et al. 2015). When compared to conventional antibiotics, the discovery and application of ZnO NPs in the treatment of fungal and other microbial illnesses in both farm animals and plants has been deemed a better alternative. The insecticide efficiency of ZnO NPs against *Artemia salina* larvae has been observed to be outstanding (Ajey et al. 2017). The biomolecules discovered in the plant extracts employed as a reducing agent can be traced back to the potential of biosynthesised ZnO NPs as an antifungal and antibacterial agent in agriculture (Jamdagni et al. 2018). Furthermore, when compared to a variety of commercially available antibiotics, the inorganic properties of ZnO NPs have the ability to endure the inhibition of microbe growth at higher temperatures and other harsh environments (Hidayat et al. 2019). The interaction and penetration of ZnO NPs into the core cells of bacteria are enhanced by their tiny size to large surface area, composition and morphological nature (Soren et al. 2018). The fertility examination of ZnO NPs in the growth of *Arachis hypogea* plant revealed a rise in seed germination, rapid shoot growth, enhanced seedling vigour index and rapid root growth; the blooming state was also fast, with a noticeable increase in pod size and yield (Prasad et al. 2012). Another investigation on the reproductive efficiency of ZnO NPs on *Solanum lycopersicum* found that germination rate and protein content increased (Singh et al. 2016). Several studies have shown that ZnO NPs can help increase the output of food crops (Liu and Lal 2015; Raliya et al. 2015; Watson et al. 2015; Zafar et al. 2016; Peng et al. 2017).

7.2 Antibacterial Activity of ZnO Nanoparticles

Zinc oxide nanoparticles come in a variety of shapes and sizes and they have outstanding antibacterial action against a wide spectrum of microorganisms (Sirelkhatim et al. 2015). According to previous studies, the antibacterial activity of zinc oxide nanoparticles improves with decreasing particle size and also increases with increasing powder concentration (Emami-Karvani and Chehrazi 2011). Nanoparticles have a strong antibacterial property due to their enormous surface area to volume ratio, which allows them to bind a greater number of ligands on their surface (Agarwal et al. 2019). The mechanism of antibacterial action of zinc oxide nanoparticles is based on induced oxidative stress. The interaction between the Zn^{+} ion and the thiol group of the bacterial respiratory enzyme induces oxidative stress in the bacterial cell, resulting in an increase in reactive oxygen species (ROS), which causes bacterial cell damage and death (Fontecha-Umaña et al. 2020). Zinc oxide nanoparticles have been found to have antibacterial action against in gram-positive and gram-negative bacteria. As an antibacterial agent, zinc oxide nanoparticles prevent food-borne and most deadly infections (De Souza et al. 2019).

7.3 Antimicrobial Activity of ZnO Nanoparticles

Because it produces free radicals, zinc oxide nanoparticles have high antibacterial action, especially on the oxide surface (Akbar et al. 2019). Because of qualities such as pressure stability, higher temperature, long shelf life and resilience, inorganic oxides outperform organic antibacterial agents. Because of their smaller size, higher porosity and larger specific area, zinc oxide nanoparticles have better antibacterial properties (Pasquet et al. 2014). The antibacterial characteristics of zinc oxide nanoparticles were used as a design principle in cosmetics, personal care items and functional textile textiles (Popescu et al. 2020). When zinc oxide nanoparticles interact with water, they produce a variety of reactive oxygen species, primarily hydroxyl radicals (OH^-) and hydrogen peroxide (H_2O_2), which play an essential role in the nanoparticles' antibacterial action.

7.4 Antioxidant Activity of ZnO Nanoparticles

Because of electron density transfer at oxygen, zinc oxide nanoparticles have antioxidant properties, which are dependent on the structural configuration of oxygen atoms (Stan et al. 2016). The naturally produced material demonstrates high natural antioxidant activity from higher plants against chronic disorders caused by oxidative processes. Zinc acts as an antioxidant by reducing cell membrane damage caused by free radicals. It also functions as a cofactor or component in a number of enzymes involved in the oxidative process. The persistent action of antioxidants causes increased sensitivity to specific types of oxidative stress. The antioxidant enzyme catalase removes peroxide from the body, and the mitochondrial membrane structure is preserved from damage (Zhao et al. 2014).

7.5 Anticancer Activity of ZnO Nanoparticles

Because of its strong solubility, effective distribution to cells and higher toxicity than individual drugs, zinc oxide nanoparticles demonstrate good anticancer efficacy. When the concentration of zinc oxide nanoparticles rises, cell viability and inhibition rise with it (Jiang et al. 2018). Zinc oxide nanoparticles inhibit ROS production in cells, causing mitochondrial membrane destruction and cancer tissue death (Medina Cruz et al. 2020). Zinc oxide nanoparticles have the ability to cause significant selective toxicity against cancer cells while causing minimal harm to normal cells (Akintelu and Folorunso 2020). Since the chemisorption of neutral hydroxyl groups over its surface, zinc oxide nanoparticles have displayed a variety of surface charge behaviour. At increasing pH, protons on the particle surface flow towards the aqueous media, leaving a partly bonded oxygen atom with a negatively charged surface behind. Protons are transported from the environment to the particle surface at lower pH levels, resulting in positively charged surface. The isoelectric point of zinc nanoparticles is 9–10, and under physiological conditions, nanoparticles have a significant positive surface charge (Mishra et al. 2017; Rasmussen et al. 2010).

7.6 Anti-inflammatory Activity of ZnO Nanoparticles

Zinc oxide nanoparticles have a higher surface area to volume ratio than bulk counterparts, making them more effective at blocking inflammation-enhancers such inflammation and cytokines (Agarwal et al. 2019). The mechanism of zinc oxide nanoparticles includes suppression of the nitric oxide synthase enzyme, inhibition of myeloperoxidase, inhibition of proinflammatory cytokines, inhibition of the NF-κβ pathway and inhibition of mast cell degranulation (Agarwal and Shanmugam 2020). Macrophages serve a critical function in the auto-regulation of the inflammatory process. There are two types of macrophages: pro-inflammatory M_1 macrophages, which increase inflammation and anti-inflammatory M_2 macrophages, which are alternately activated as a response to anti-inflammatory reactions and rebuild the afflicted organs and tissues' processes.

7.7 Antidiabetic Activity of ZnO Nanoparticles

Zinc oxide nanoparticles have a remarkable anti-diabetic impact, including improved glucose tolerance, lower blood glucose, greater serum insulin, lower non-esterified fatty acid levels and lower triglycerides (Raguraman et al. 2020). Zinc is well-known for its role in the biosynthesis of insulin production and storage, and it is found in the structure of the hormone. Zinc transporters in the pancreas' β-cell, such as zinc transporter-8, have been found to play a key role in insulin secretion. Zinc improves insulin signalling via increasing phosphorylation of insulin receptors, increasing phosphoinositide 3-kinase, and increasing phosphoinositide 3-kinase. As a result, there is a complex interrelationship between zinc and diabetes. Zinc oxide nanoparticles show a considerable reduction in fasting blood glucose levels in diabetics (Siddiqui et al. 2020).

7.8 Photocatalytic Activity of Zno Nanoparticles

The photocatalytic activity of zinc oxide nanoparticles demonstrates increased electron mobility, which increases the rate at which zinc oxide electrons are photogenerated, which prevents photogenerated holes and electrons from recombining, resulting in an increase in the lifetime of photogenerated charge carriers. The photocatalytic reaction rate can be increased through a variety of means, including decreasing the bandgap, increasing defect concentration and increasing surface area (Hanif et al. 2019). As the pollutant concentration rises, so does the photocatalytic activity, and as a result, the likelihood of the lit light beam reaching the catalyst particles decreases. Because zinc oxide nanoparticles have a larger surface area, a narrower bandgap and a smaller particle size, they absorb more UV light and decompose more quickly. As a result of the photocatalytic activity, the production of smaller nanoparticles is boosted (Munshi et al. 2018).

7.9 Wound Healing with ZnO Nanoparticles

Wound healing is an active process in which wounded tissue is replaced to its pre-injury state and the injured area is depleted in a clear evidence of healing (Khalid et al. 2017). Metal oxide nanoparticles produce reactive oxygen species, which aid fibroblast growth significantly. The surface area and particle size of zinc oxide nanoparticles influenced the interlinking of fibroblast cells with nanoparticles. Increased particle size boosts cell growth and membrane integrity (Kaushik et al. 2019). Myofibroblast activity causes wound contraction, which minimises wound area. The hydrogel-based wound dressing improves re-epithelialisation by increasing contact time and following keratinocyte migration (Mihai et al. 2019). Through wound healing, zinc oxide nanoparticles promote apoptosis, bacteria clearance, platelet activity, tissue necrosis, re-epithelialisation, tissue scar formation, debris elimination, angiogenesis and stem cell activation (Batool et al. 2021).

7.10 Degradation of ZnO Nanoparticles

Several investigations on the use of biosynthesised ZnO NPs as dyes and other inorganic waste degrading instruments, particularly in textiles, waste water and municipal effluents, have been published (Azeez et al. 2018; Jose et al. 2017; Rana et al. 2016). The degradation efficiency of ZnO NPs generated utilising *Petroselinum crispum*, *Allium cepa* and *Allium sativum* on methylene blue dye was compared, and it was discovered that all of the synthesised ZnO NPs can degrade methylene blue dye. When compared to regular zinc oxide, the degrading effectiveness of ZnO NPs against the dye was attributed to their smaller size, which increased the number of reaction sites on the catalyst surface (Stan et al. 2015). A crucial factor determining the degrading efficiency of ZnO NPs was discovered to be the ratio of catalyst loading to dye concentration. According to a report, the degradation efficiency of ZnO NPs is inversely proportional to the dye concentration used, because increasing the dye concentration in the solution reduces the path of photons entering the solution, lowering the amount of holes and radicals required for the degradation process (Suresh et al. 2015). Because each structure has a different degree of reaction site, the findings show that morphological aspects of ZnO NPs have an impact on degrading efficiency. In a study of the photodegradation effectiveness of ZnO NPs toward Alizarin Red-S dye employing produced ZnO NPs with various structures, it was discovered that ZnO NPs with nano-flowers had the best degradation efficiency compared to other ZnO NP structures (Sharma 2016).

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Biomolecule Integrated Nanostructures for Advanced Diagnosis Systems in Viral Disease Management of Crops

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1 Introduction

1.1 Plant Virus as a Threat to Food Security

The year 2019 will be itched in the history of the human race for the novel coronavirus strain that drew the attention of every social and electronic media platform since the pandemic caused by the virus resulted in many life losses in many first-world countries. The pandemic was later declared as a global threat by WHO and the result was seen throughout the globe in the form of human isolation, social restriction, and lockdown. The multidimensional impact of the single virus strain on health and socioeconomic status is going to haunt human civilization for the next couple of decades. The pathogenic virus strain not only plays an ultimate role in the human health sector but also in other fields such as agriculture, farming, and food processing industry sectors.

Many plant viruses have been reported as a threat to food security and hamper the agroeconomy. In 1988, a novel virus causing cassava mosaic disease emerged in the East African country, Uganda which was later named as East African cassava mosaic virus (EACMV-UG). This virus group was instantly blown out to all over East and Central African countries by whiteflies. As EACMV-UG went berserk, it demolished the farmsteads of cassava in diverse nations pan Africa, ensuing in farmers abandoning the crop and instigating food crisis and correlated genocide

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(Legg et al. 2006). Crop diseases caused by viruses hinder the growth and developmental phases of plants and thus reduce their yield and productivity. It not only spoils crop production but also affects post-harvest productivity and thus affects the overall income of the farmer. Such harvest forfeitures emerge universally, triggering impairment erratic as of diminutive degree to entire crop catastrophe (Farooq et al. 2021). Developing countries from Asia, Africa, and South America where the economy and the social structure depend strongly on agriculture cannot afford the burden of crop loss or failure as the people's livelihood is webbed with the agricultural yield. Therefore, damage to crops either by pests, fungus, or viruses will have consequences on the gross domestic product (GDP), which is a matter of gross concern for a country. The emergence of viruses like cassava mosaic virus (CMV) that causes huge losses in the production of cassava, the third most important crop in tropical regions in the 1980s was not a single event. There are over 1000 virus species known to infect plants and around seven orders of the class of insecta that transmit plant viruses. Therefore, plant viruses and agricultural epidemics due to plant viruses are rampant and can lead to crop losses that severely affect a region's food security. Plant virus epidemics such as the one caused by EACMV-UG are particularly devastating when they affect staple crops like cassava. There are 15 staple crops listed by FAO which afford 90% of the planet's vital energy food resources. Rice, maize, cassava, potato, wheat, sorghum, rye, lentils, oats, teff, soybean, and sweet potato are all listed by FAO. In temperate areas, the damaging effect of viral infection triggers crop losses, particularly in the biobased, well-managed farming system along with those farmlands which have a tendency to happen further recurrently in secure harvesting schemes (Kashyap et al. 2016). They arise not only in staple crops but also in vegetable-yielding plants, fodder plants for livestock, and also in medicinal or commercially valuable plants.

1.2 Current Diagnosis Systems for Virus Detection

Diseases caused by viruses often jeopardize innate ecology by triggering the fluctuation in the species constitution of floral populations. The viral diseases not only induce genetic attrition, but their adverse effect also influences plausibly heading toward complete extinction of the species (Jones and Naidu 2019). Ever rising temperature of the earth due to issues of global warming and the climate instability induced by the global warming phenomena is further creating epidemics additionally challenging to manage (Trebicki 2020). The effects of climate change and global warming apart from jumping viruses among organisms are influencing the ecological triangle between the plants, plant viruses, and their insect vectors, with each factor influencing the other two. Rising temperatures, in particular, exert a strong influence on all three elements of the virus-disease triangle and the world has been getting warmer every year. As temperatures increase, plants, viruses, and insects will migrate seeking their preferred temperatures along with the variation in crop pattern and land and weather conditions. In general, these migrations will come into contact with new indigenous species, with each encounter moving with it the probability of a novel plant virus epidemic. The effect of climate change and global warming will also increase the virulence and frequency of outbreaks of known plant viruses. Therefore, it is not overstated to consider the need for suitable preventive measures in diagnosis as well as finding suitable treatment against the plant virus diseases, before they spread into noninfected plants. Plant viruses are chiefly composed of a core unit of nucleic acid carrying genetic information, which is further securely encompassed by means of an exterior cover of proteins. Most of the viruses that infect plants, somewhere around 90 out of each 100 pose genome that is composed of RNA coupled with the DNA genome with either a solo coil of single-strand or double-helical form in residual 10% members (Blawid et al. 2017). These biological units are recognized as obligate parasites for their potential toward instigating infections, which results in diseases within complete biodiversity that includes plants, animals, bacteria, protozoans, and fungi. Plant viruses infect and transmit through plant saps, insects, protists, soil-borne nematodes, pollens, and also through human interference. They intervene in the nutrient resources inside the plant cells. They attack the host system, infiltrate their defense system, alter the developmental pattern, trigger changes in the growing and aging pathways, as well as eventually command senescence and cell death. Many observed symptoms of viral infection include chlorosis, necrosis, mosaics and yellowing of leaves, mottled and crinkled leaves, and deformation in leaves, flowers, and fruits to name a few. In spite of this, certain viruses, underneath adequate situations, are capable of debauching a species in default of establishing the signs of infection (Schumann and D'Arcy 2012). Based on the loss caused by plant pathogens in crop productivity worldwide, plant virus diseases are placed next to fungal pathogens in terms of economic loss. The harvesting loss rooted in viral pathogen-related ailments remains arduous in the direction of prefiguring due to different factors (Ellis et al. 2008). The severity of the pathogenicity relies on several factors like the strain of the viral isolate, host system cultivar, geographical distribution along with the period of transmission (Strange and Scott 2005). Adding to this, the indications and signs of viral transmission can be misperceived alongside further pathogen infections, environmental stress factors, signs of climatic variation, or otherwise imbalances due to nutrition-related issues, which have quite identical resemblances in signals. All these factors make it difficult to identify the disease. As a result, the identification of diseases caused by viral agents centered on the witnessed indications or signs is furthermore challenging than those diseases initiated by erstwhile pathogenic agents (Van der Want and Dijkstra 2006). The removal of restrictions on agricultural trading and the opening of the import–export market along with climate change leads toward the evolution of old viruses and the appearance of various noble plant viruses. Their diagnosis and identification are a new challenge in the present time. Prevalent modus operandi similar to that of enzyme-linked immunosorbent assay (ELISA) along with polymerase chain reaction (PCR) yet holds good in detecting plant-based viruses. These methods use complementary nucleic acid or antibodies and specifically bind with the target viruses using hybridization-based or PCR-based systems. These detection methods although have a higher affinity toward known viruses but do not have the capability to diagnose those viruses which remain ahead of their spotting range or which strains are recently evolving. Contrariwise, the instrumentation and the reagents for such detection methods are costly, time-consuming, and need expert handling to get the correct results. In lieu of these accounts, it evidences a challenging task toward application and implementation of these approaches on-site. In addition, these applications cannot be performed excluding expertized analytical laboratories, these hindrances motivate toward the advancement of state-of-the-art identifying approaches with quite a few restraining elements. The search for adaptive, cost-effective, and efficient diagnostic kits or assays has been reconnoitered in numerous respects (López et al. 2008). Recent advances in the usual PCR and induction of novel amplification techniques like loop-mediated isothermal amplification (LAMP) recompense the major shortcomings of the prevailing PCR-based approaches. As well as it is acknowledged for its ability to amplify target nucleotide sequences at a faster rate with higher specificity and sensitivity (Notomi et al. 2015). Alternatively, fluorescent proteins, owing to their advancements of easy observation and biocompatibility and lesser toxic effects, are capable of applicability in several areas for instance trafficking of biomolecule through membranes, identification of pathogenic strains, along with quantifiable measurements of protein/RNA expression (Berg and Beachy 2008). Conversely, the narrow excitation wavelength ranges of fluorescent protein due to the presence of organic groups limit the detection range.

1.3 Nanodiagnostics Applied to Virology

The identification of plant disease is the foremost step in finding the pathogen including the plant virus that causes the infection. Correct diagnosis, therefore, represents the main module in managing plant diseases. Early detection of disease or the causal organism plays a central role in reducing harvest damage. Killing or burning down the harvest can be a poor option, on the other hand, the use of pesticides, insecticides, or anti-viral treatment after the identification of diseases can inflate the cost and also cause toxicity along with environmental risks. Out of all known plant-based diseases, viral diseases are more complex in detection, diagnosis, and control. Therefore, many strategies are being evaluated in plant-disease management, particularly those representing viral diseases like arresting the early stages of infection during replication of virus or formation of viral proteins. Nanodiagnostics tools in this regard can be immensely useful. The identification of viruses founded on nanostructures along with the exploration of biomarkers together with the advancement of multiple detection kits is crucial in spotting viral pathogens. Different variants of viruses or morphologic, metabolic, or physiologic changes can be explained on the basis of their genomic or proteomic expression profile on healthy and infected samples. State-of-the-art techniques for detecting viruses are critical in disease management (Aboul-Ata et al. 2011). A detection system ought to be more precise, user-friendly, accurate, giving unambiguous results, and ultrasensitive (McCartney et al. 2003). Therefore, nanotechnology that deals with nanoscale size can be surely utilized as an appropriate technology in the development of smart materials, nanoscale devices, or equipment that can detect and diagnose plant viruses accurately with a minuscule sample volume. Faster diagnosis, better recognition, and monitoring of regulatory molecules like micro-RNA, DNA, or peptides depend on their detection sensitivity with a nanodiagnostic sensor system (Wang et al. 2006).

1.4 Onsite Application Systems Based on Nanosensors

Nanotechnology-based equipment can be applied both in the lab or in the field. The field-based or onsite-based nanodevices have the advantage of direct analysis, unlike the other one where the samples are to be collected, transported, and analyzed routinely in a laboratory. Such field-based nanodiagnostic systems can smartly monitor the timespan of crop planting to harvesting, climatic condition, humidity, soil nutrition, and organic and inorganic matters including viruses. These nanomachines are made up of stable organic materials like polyaniline, polythiophene, or polypyrrole and are able to utilize real-time global positioning system (GPS) or satellite images for the record and transmit using wireless sensors to appropriate centers for analysis (Prasad et al. 2019). Nanosensors not only efficiently spot the diseases prior to notable signs start giving the idea but also alleviate in controlling the spread. Preventive and protective farming practices against plant diseases allow for higher agriculture productivity and help farmers getting higher agricultural output and hence make better financial gains (Rai and Ingle 2012). Figure 1 gives an account of general approaches used in the current scenario for detecting crop viruses.

2 Nanobiosensors as a Diagnostic System

2.1 Nanowires/Nanofibers Coated with Biomolecules for Plant Virus Detection

A nanowire (NW) is a nanoscale structure like a wire with a diameter in the order of nanoscale (10−9). The ratio of length to width in nanowires is in the range of 1000 or more. The progress in nanomechanical characterizing methods in current years, specifically in situ electromagnetic (EM) techniques, has advanced momentous growth in understanding NW mechanical behavior. The properties of nanowires include elasticity and plasticity of the structures and having sufficient tensile strength to withstand pressure (Ambhorkar et al. 2018). This quality makes the nanowires a robust candidate for nanobiosensors. Biomolecule-derived nanowires like in the case of bacterial nanofibers are now under investigation for the detection and diagnostics

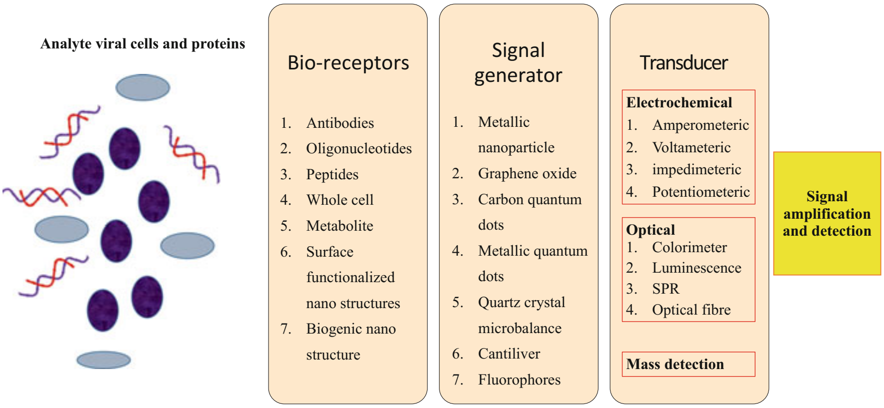

Fig. 1 Schematic representation of different approaches in nanosensor development currently in practice for detection of crop virus. Components of nanobiosensors, different analyte molecules (whole cells, viral proteins, and nucleic acids) the whole cells are purple spheres, and light blue oval-shaped surface proteins and coat proteins, and nucleic acids of DNA strands, capturing bioreceptors (surface-functionalized antibodies, peptides, nucleic acid probes, and hybrid probes) optical transducers, and signal amplifiers (nanostructures, plasmonic dots, quantum dots, fluorophores, nanocrystals, nanodiamonds, quartz crystal microbalance, and cantilevers) and other detectors like mass detectors

of diseases (Yuan et al. 2020). Bacterial or microbial nanowires are electrically conductive nanoappendages produced by anoxygenic *Geobacter* and *Shewanella* genera of prokaryotes. Being extensively used in carbon and metal cycling, the electrically conductive bacterial or microbial nanowires provide multiple applications including disease detection. These nano-appendages were well studied in anoxygenic *Geobacter* and *Sheawnella* species where the electrical conductivity is generated through the pili and dried cytochrome-rich membrane extensions respectively (Ptushenko, 2020). Apart from sulfate or metal-reducing bacteria, cyanobacterium such as *Synechocystis* PCC6803 or oxygenic *Pelotomaculum thermopropionicum* alone or in association with archaea like *Methanothermobacter thermoautotrophicus* can yield electrically charged nanowires with varied application in biological communities (Filman et al, 2019). These nanowires use the enzyme cytochrome oxidase for electron transfer and energy coupling. The application of these bacterial nanowires holds significance mostly in energy conversion and in the bioremediation process. Protein nanowires harvested from microbes like *Geobacter* can produce biological memristors that can fluctuate under voltage range and possibly act as bio probes. Such voltage-responsive signals can be recorded, if required amplified, and integrated with specific biological analytes for the detection of pathogenic strains by sensing redox changes (Fu et al, 2020). Nanowires with conductive properties are key elements in nanosensors. They have advantages like having a high surface-to-volume ratio, comparable Debye length with the target molecule, and easy integration with gadgets or electronic devices. Physical properties like tensile strength and elasticity stability over a range of temperatures are also considered important for sensor application. In contemporary years, attention was given to the development in the fabrication of one-dimensional metal-augmented conductive nanowires from DNA scaffolds. DNA is known to have poor electrical conductivity and this is counteracted by framing metal nanowires around the DNA. This metal-wrapped DNA acts as a template platform for forming conductive wires of gold, silver, or palladium (Ye et al. 2019). Another method to make an electrochemical nano biosensor is using the rolling circle amplification (RCA) approach in which deoxyribonucleic acid (DNA) is made attached with gold nanoparticles (AuNPs) to generate conductive nanowires. Such electrically conductive metal nanoparticles act as electrodes and are able to produce electrical signals when coming in contact with specific target DNA sequences. Nano biosensor fabricated using the RCA method has been found to electrically sense up to 10ng of Escherichia coli (E. coli) genomic DNA with a high signal-to-noise ratio, which is required for better specificity in the detection of E. coli genomic DNA (Russel et al, Another method to make an electrochemical nano biosensor is using the rolling circle amplification (RCA) approach in which deoxyribonucleic acid (DNA) is made attached with gold nanoparticles (AuNPs) to generate conductive nanowires. Such electrically conductive metal nanoparticles act as electrodes and are able to produce electrical signals when coming in contact with specific target DNA sequences. Nano biosensor fabricated using the RCA method has been found to electrically sense up to 10ng of Escherichia coli (E. coli) genomic DNA with a high signal-to-noise ratio, which is required for better specificity in the detection of E. coli genomic DNA (Russel et al, 2014). In such methods, the DNA is either fixed over a flat surface or in an aqueous solution forming in-plane or out-of-plane nanowires. RCA creates a long single stretch of repeated DNA sequence that is shaped from a circular DNA template expressed through a DNA polymerase enzyme on an electrode. This linear DNA thread is hybridized with gold nanoparticles, which results in the synthesis of metal-based DNA nanowires that are used in the fabrication of electrical devices and applied in the field of biological sciences. The verification of nanowires can be tested using any one of these methods like scanning electron microscopy (SEM), confocal microscopy, and electrical conductivity measurements (Guo et al. 2018; Karnaushenko et al. 2020). Nanowire biosensors are a subgroup of nanosensors, whose prominent sensing portion consists of one-dimensional nanowires enveloped by nanosized biomolecules such as small DNA or RNA molecule, peptides, or proteins. The surface properties of such nanowires can be altered or modified using any potential biological marker or unique recognition motifs that can specifically identify different target molecules. As an example, the thiol-containing compound 11-mercaptoundecanoic acid can modify the surface of nanowires by forming a self-assembled monolayer (SAM) that can bind to anti-maize chlorotic mottle virus (anti-MCMV) for detection of MCMV disease. This surface plasmon resonance (SPR) sensor response has a dynamic range of MCMV detection is up to 1 to 1000 parts per billion (ppb) and it is observed that it can detect much better than ELISA based method (Zeng et al. 2013). Nanowires as transducers make a better sensing device to identify cucumber mosaic virus (CMV) and papaya ringspot virus (PRSV), which makes them a suitable material for viral disease detection (Ariffin et al. 2014).

Biobased sensing devices that rely on living cells are also featured with ultrasensitivity having a low detection limit, higher specificity, and faster response time. Another approach in detecting plant viruses like potato virus Y (PVY), CMV, and tobacco rattle virus (TRV) is to immobilize virus-specific antibodies on the surface of a portable nanobiosensor system. Developing such a biobased system using nanowires or nanofibers for application in the agricultural field is getting recognized and shows the possibility for wider application (Perdikaris et al. 2011).

2.2 *Quantum Dots (QDs) Conjugated with Biomolecules*

QDs are man-made nanoscale semiconductor devices that emit fluorescence when stimulated by a suitable wavelength of the light source. Such precursor elements of QDs belong to groups II and VI or groups III and V of the periodic table. Apart from metallic precursors, many other compounds can become the precursor for the generation of QD-based sensor devices that have excellent optical properties. It includes living cells, biomolecules, and chemical compounds with unique structure and binding regions when conjugated with zero-dimensional quantum dots (QDs). Such biomolecule-based QDs (also known as biodots) are novel class quantum dots that have high photoluminescence signal capability, better management under an aqueous environment, compatible with wide systems, high scalability, and better programmability when compared to the metal-based QDs.

Another group of QDs is labeled as carbon QDs and graphene QDs, which have sizes below 20 nm. They are chemically inert, permeable to biomembranes, adaptive toward different functional groups, water soluble, and also low in toxicity. Due to the above properties, such QDs are used in the field of bioelectronic devices and energy transformation systems (Molaei 2020).

Overall, the QDs exhibit higher adaptability, compatibility, scalability, and low cost when compared to conventional semiconductor QDs. Because of these features, QDs now have wide applications in detection and diagnostics. In the same line, different biomass of bacteria, fungi, or algae, plant and plant part extracts, and biological macromolecules (like sugars, organic acids, DNA, RNA, and small peptides) have been used in the assemblage of signaling QDs.

Carbon or graphite quantum dots are eco-friendly and have structural properties that can be used in biosensing with high sensitivity, selectivity, and reproducibility. Due to better optical properties, such QDs can detect cytogenic and biomaterials with higher accuracy (Ji et al. 2022). In the last few years, different methods have been employed in the preparation and fabrication of quantum dots. Two approaches top-down and bottom-up are employed for this purpose. In the top-down approach, fabrication of carbon or graphene-based QDs works on the basis of breaking larger parts of molecules into smaller parts and involves methods such as solvothermal synthesis, electrochemical degradation, nanolithography, electrochemical and acidic oxidation, arc discharge, laser ablation, and chemical exfoliation for their synthesis. In contrast, the bottom-up approach uses an assemblage of smaller units into larger groups and involves methods such as microwave irradiation, hydrothermal synthesis, ultrasonication, and pyrolysis (Mhlanga and Tetyana 2021). Moreover, QDs are advantageous over other nanomaterials in having a fluorescence signal in the precise signal-noise ratio. Along with this, the QDs are considered more efficient compared to traditional organic fluorophores in detecting the fluorescent marked DNA or proteins (Adams and Barbante 2013; Holzinger et al. 2014). Predominantly, viral nucleic acid-based hybridization assays are employed in antigen–antibody interaction for working immunoassays as machinery for the nanosensors. Such interactions between these biological molecules will enable FRET (Förster resonance energy transfer) to perform in which the excessive energy of the excited molecule is transferred between the donor and the acceptor fluorophore molecule (Shi et al. 2015). An example of quantum dots FRET-based biosensors has been used in detecting *Polymyxa betae* (Keskin) transmitted necrotic yellow vein virus (BNYVV) that is known to cause rhizomania disease in the sugar beet plant. In this regard, the quantum dots FRET-based biosensors are made to be conjugated electrostatically under an aqueous environment between the antibody of protein glutathione-S-transferase (Ab-GST) and thioglycolic acid-modified cadmium-telluride QDs (CdTe-QDs). This conjugated structure acts as an energy donor for the FRET-based biosensor. On the other hand, the fluorescent dye rhodamine attached to glutathione-S-transferase (GST) acts as an energy acceptor. The formation of the donor–acceptor complex (QDs-Ab-GST-rhodamine) allows the dye and QDs to participate in FRET. Such immune-based nanosensors provide better opportunities in detecting plant-based pathogens (Safarpour et al. 2012). Similarly, in the diagnosis of citrus tristeza virus (CTV), the cadmium telluride-quantum dots are conjugated with a specific antibody against the coat protein (CP) of CTV. The coat protein is then immobilized onto the gold nanoparticles (AuNPs) surface to complete the structure. This structure leads to the development of a highly specific fluorescence resonance energy transfer (FRET) supported nano biosensor (Shojaei et al. 2016a, b). The above-mentioned set of energy acceptors and donors has also been experimented in another study by the same group in which the conjugated quantum dots are immobilized on the surface of carbon nanoparticles (CNPs). With this experiment, the capability of viral recognition and sensitivity is found to be further enhanced (Shojaei et al. 2016b). Presently, two quantum dot-based methods, FRET-based and FRET independent methods provide opportunities for plant virus detection in infected plants. As mentioned above, the fluorescence resonance energy transfer (FRET) based assay depends on the quenching ability of rhodamine molecules, which alters the light emission of QDs. Alternatively, in the FRET independent method, the CTV antibody-QD particle solution (Ab-QD) is added with free antigens that cause aggregation or clubbing resulting in the formation of Ab-QD conjugates. This agglomeration of Ab-QD conjugates increases the light emission intensity of the QDs for detection (Safarnejad et al. 2017). Both of these approaches will find relevance in years to come in detecting multiple and variable forms of plant virus or pathogens in crop diseases.

2.3 Gold Nanoparticles from Biomolecules

Gold nanoparticles (AuNPs) are one kind of nanoparticles belonging to the group of metallic nanoparticles. Gold nanoparticles are used in sensing molecules, delivery, and biocompatible conjugation with other molecules. Except for biodegradability, gold nanoparticles have excellent optical and electronic stability along with macroscopic quantum tunneling and the presence of SPR bands. All these features of gold nanoparticle-based structures make them a suitable candidate for the preparation of suitable nanobiosensor molecules (Li et al. 2010; Biju 2014). Majorly, transmission electron microscopy is used to detect the interaction between the nanoparticles and their biospecific interaction. In addition to established colloidal gold nanoparticles structure that is nanospheres, other nanostructures like nanorods, nanospheres, nanoshells, nanocages, and nanostars are among the other configurations that are applied in different biospecific interactions (Khlebtsov and Dykman 2010). In this context, small oligomeric DNA can be intertwined with diverse shapes of self-assembled gold nanoparticles resulting in the formation of diverse conformations. Such probe conjugated gold nanoparticles are able to detect colorimetrically single-strand DNA of the tomato leaf curl New Delhi virus (ToLCNDV). Advancement of such scanometric based nanoassay that involves direct or sandwich hybridization method puts forward novel development of biosensors for plant-based virus detection (Dharanivasan et al. 2016). In another report, instant diagnosis of viral infection caused by tobacco mosaic virus (TMV) can be detected visually through an immunochromatography technique using colloidal gold nanoparticles on poly composite test strips (Drygin et al. 2009). Another approach uses lateral flow assay (LFA) in which the movement of sample or analyte takes place over a paper or strip containing an absorbent pad. The detection of the sample or analyte by the reporter molecules releases a visual signal that can be optically detected. This method is used to detect soybean mosaic virus (SMV) in the infected leaves and seed samples of the soybean plants (Zhu et al. 2016).

2.4 Nanorods and Nanoribbon Technology

Nanorods and nanoribbons offer an advantage over nanospheres in having more enhanced signal generation with less background noise ratio. The spectral properties of gold nanorods are found suitable for biosensing purposes due to their low absorption of nonspecific biological buffers and also a minimal scattering of endogenous chromophores (Nusz et al. 2008). Specifically, gold nanorods (AuNRs) possess better sensitivity toward the dielectric environment (McFarland and Van Duyne 2003). Due to the unique optical properties of AuNRs, these candidate molecules are recognized in the making of ultrasensitive and highly specific optical transducer nanosensor kits. Such kits are capable of detecting disease-causing bacteria in the host cells (Parab et al. 2010) and also as Raman labels in a sandwich immunoassay for detecting viruses (Baniukevic et al. 2013). The gold nanorods that are immobilized on the fiber optic particle plasmon resonance (FOPPR) immunosensor are shown to provide rapid diagnosis against cymbidium mosaic virus (CymMV) or odontoglossum ringspot virus (ORSV) (Lin et al. 2014a, b). The detection of those viruses is performed on crude sap exploiting the immunosensor, which is connected by gold electrodes over the quartz crystal microbalance (QCM). Any change in frequencies of the QCM resonator on such nanosensor can be measured and provide information on the presence and absence of pathogen. On a similar ground, chemiresistive sensors fabricated on antibody-functionalized polypyrrole (PPy) nanoribbons can detect viral pathogens by responding to changes in the nearby chemical environment. This method uses lithographically imprinted nanowire electrodeposition (LPNE) techniques to detect plant virus-like CMV (James 2013). In such cases, CMV-specific antibody is conjugated on the surface of N-ethyl-N′-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC)/N-hydroxysuccinimide (NHS) and that is batch fabricated onto the PPy nanostructured biosensor. It becomes crucial to understand that the internal and external factors that control the detection limit should be optimized and made compatible with biological systems for better detection efficiency. In the above nanobiosensor, the detection of the virus is reappropriated by adjusting the electrical conductivity of PPy nanoribbons, by altering the aspect ratio of nanoribbons, and also by changing the buffer environment on which the nanobiosensor works (Chartuprayoon et al. 2013). Overall, a nanobiosensor-based pathogen detection system is a modern strategy for recognizing viral diseases and this approach can detect early symptoms. Such nanobiosensors have the potential to be mass manufactured and can be used for detecting pathogens in crop fields.

3 Biological Agents Based Sensors

The involvement of a biomolecule as the detection agent in different analytes that are transduced with the help of optical or energy transducers for signal generation is key to sensor development and fabrication. The signal generated through this is further enhanced with the signal amplifying molecules like colloidal gold/silver nanoparticles with colorimetric detection or organic fluorophores for FRET-based detection methods. Such biomolecular interaction-based point of care (POC) instruments can be fabricated for the spotting of several viral molecules. In this regard, the nature of the biomolecule can be a criterion for characterization. Many antibodies-based immune sensors, nucleic acid-based sensors, and liposome or lipid dendrimer-mediated nanosensors have come into the consideration in recent past. This subsection will emphasize those biospecific nanosensors for viral detection and diagnosis in crop plants.

3.1 Immunosensors or Immunochips

In the current diagnostic situation, antibodies (Abs) have become key affinity ligand molecules because of their production capabilities against any kind of molecules be it small drugs, receptors, or even intact cells. It is generally considered that making an antibody, either polyclonal (pAb) or monoclonal antibody (mAb) along with quality control and maintenance is challenging and is paramount in making a lasting and sensitive molecule for experimental method. However, with evolution in recombinant science techniques, it is now manageable to achieve heterologous expression of recombinant antibodies (rAb). For example, single-chain variable fragments (scFv) and the antigen-binding fragment (Fab) have the specificity at par with that of mABs. These antibodies are also cost-effective and constructed mainly from hybridomas. It is not easy to obtain pathogen-specific antibodies as the antibodies can cross-react with protein and carbohydrate epitopes present on the surface of intact cells of different species. To present such cross-reaction of antibodies with multiple epitopes, it should be made directed against a single target molecule. Such target molecules are constitutively expressed and found on the surface of the membrane for easy detection and binding. Researchers explore, clone, and express numerous pathogen-specific surface proteins and use them as suitable antigens for the assembly of antigen-specific antibodies with better target specificity. Such methods have proven successful in generating species-specific antibodies that help in building immunosensors. In building immunosensors, the specific antibodies or antigens can be made coupled with a transducer or a signal molecule that can be detected with the generation of an analytical response. Immunosensors are further categorized into four on the basis of signal transduction methods. They are electrochemical sensors, optical-based sensors, piezoelectric based, and thermometric based. Out of these four groups of immunosensors, the electrochemical-based one is promising in detecting viral antigens due to higher sensitivity, better speed of detection, and lasting response. Using this method, a portable electrochemical-based immunosensor system has been tested for identifying CMV in which the CMV-specific antibodies adhere with gold nanoparticles (AuNPs) are used. Such electrochemical immunosensor provides valuable information in terms of real-time data and higher sensitivity toward detecting CMV in the field of nanopathophysiology (Rafidah et al. 2016). Recently, a label-free and sensitive electrochemical immunosensor is reported for fast detection of citrus tristeza virus (CTV). In this case, a specific antibody is generated against the viral coat protein (CP) of CTV and is successfully immobilized on 11-mercaptoundecanoic acid (MUA) and 3-mercapto propionic acid (MPA) modified gold electrode via carbodiimide coupling reaction using N-ethyl-N′-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxy succinimide (NHS) (Haji-Hashemi et al. 2017). In another example, an immunosensor is developed for effective and specific detection of capsicum chlorosis virus (CaCV) collected from infected bell pepper plant leaves. Here, the viral antigen is immobilized over the gold nanoparticle/multiwalled carbon nanotube (nano-Au/C-MWCNT) surface. It is followed by the addition of electrodes on the surface of the nanoparticle/nanotubes (nano-Au/C-MWCNT) formation an nanoimmunosensor. This immunosensor is cross-linked with N-ethyl-N′-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC)/N-hydroxysuccinimide (NHS) and incubated for some time followed by the addition of groundnut bud necrosis virus (GBNV)/capsicum chlorosis virus (CaCV) specific polyclonal antibody. This interaction between immobilized antigen and polyclonal antibody is directed for label-free redox detection and found 1000 times more sensitive than the classical methods like ELISA (Sharma et al. 2017). Similarly, for label-free detection against orchid viruses, a highly sensitive biosensor has been developed using anodic aluminum oxide (AAO). The barrier layer of AAO is altered for deposition of thin gold (Au) film followed by electrochemical deposition of Au nanoparticles. This 3D nanostructured sensing electrode is formed with the uniformly distributed gold nanoparticles over the AAO barrier layer, which utilizes a detection mechanism based on electrochemical impedance spectroscopy (EIS) to quickly identify the odontoglossum ringspot virus (ORSV) strength from the infected leaves of orchid plants. In this method, the ORSV antibody (anti-ORSV) is immobilized on the nanosize surface with electrodes that forms a self-assembled monolayer (SAM). With specific antigen–antibody binding, the nanobiosensor provides accurate results by indicating interfacial charge transfer resistance on the electrode. This indicator gives a fast and accurate signal that allows one to

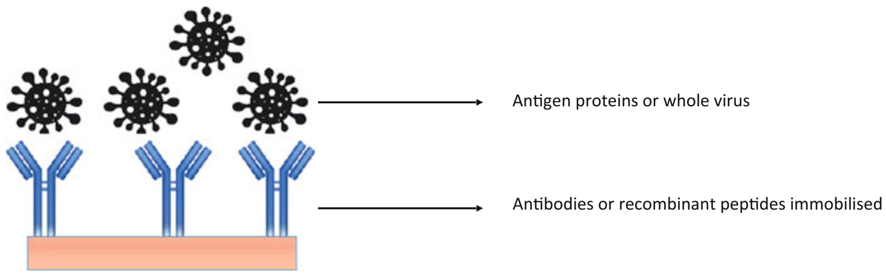

Fig. 2 The immobilized antibodies or modified proteins are allowed to react with the specific antigens resulting in electrochemical detection or colorimetric detection

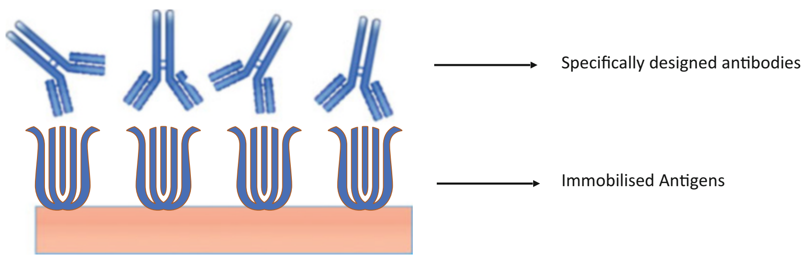

Fig. 3 The immobilized specially fabricated antigens are specific for particular antibodies (adapted from Saylan et al. 2019)

distinguish between the healthy and the leaves of the infected orchid. This report on ORSV detection is also feasible for field applications in agricultural plots (Jian et al. 2018). A representative figure of immobilized antibodies binding with specifically designed antigens is shown in Fig. 2 and immobilized antigens binding with specifically designed antibodies in Fig. 3.

To detect the plant virus there is a need to have assemblages of detection setup in the form of nanosensors. Antibody immobilization on sensor surfaces is crucial for biosensor sensitivity. In this regard, surface chemistry plays a vital role by allowing the optimal orientation, proper conformation, distortion-free binding of antigen–antibody, and higher angle of free rotation for antibodies for providing further signaling responses. Various methods are available for antibody immobilization but the optimization for each individual system is desirable for the proper functioning of such applications. The surface of the sensors is usually consisting of inorganic substances like glass and metallic compounds like gold, iron oxide, and platinum on which the surface modification is carried out. There are two approaches used for surface modification or functionalization, direct physical adsorption and the second is using a covalent attachment. In both methods, applying standard wet lab techniques the organic biomolecules are deposited and immobilized over the inorganic substances, metallic plates, or silica surface. Compared to the direct physical absorption method, the covalent attachment proves to be advantageous as it allows ligands to maintain their conformational rigidity and adhesive property and prevents leaching out from the surface. Two-dimensional surfaces such as organosilanes, self-assembling monolayers (SAMs), dendrimers and polyethylene glycol (PEG) brushes along with three-dimensional surface supports system like agarose, aldehyde–agarose, and carboxymethylated dextran have been extensively used as binding surface material and provide a platform for the evolution and assemblage of novel nanobiosensors (Álvarez et al. 2018).

Another approach in the immunosensor category falls under the group of quartz crystal microbalance (QCM). Quartz crystal resonators are known for their stability and precise oscillations. Due to this, they are used in the measurement of frequency changes and therefore play role in the making of QCM-based sensors (Torad et al. 2019). Also, the crystals of quartz are easily available, cheaper, and sturdy in nature. QCM sensors buildup of thin quartz discs with electrodes attached over them and when an oscillating electric field through those electrodes is given, it tends to oscillate at a defined frequency. The frequency of oscillation varies with the addition or removal of mass onto the electrode surface and the quantification of frequency remains constant over a wide dynamic range. This change in frequency provides useful information regarding biomolecular interaction, antigen–antibody binding, and surface chemistry. One example of QCM immunosensor where the orchid pathogenic virus is detected rapidly through 3,3-dithiopropionic acid-based self-assembled monolayer (SAM) where the nanosized gold crystals and the antibody are attached to the sensor surface (Skottrup et al. 2008).

Another group of biosensors that uses atomic force microscopy (AFM) for surface sterilization is a cantilever-based technique that has a sharp tip structure to investigate the surface. In a recent study, AFM is applied in microfabricated cantilever-based sensors functionalized with suitable antibodies for testing purposes. Cantilevers are mostly maneuvered in stationary mode and the static mode detection happens when the dynamic changes in the analyte are measured by the static bending of the cantilever. Conversely in dynamic mode, the cantilever measures the resonance energy changes in analytes that are bound to the surface in an equivalent manner to that of the QCM sensor. Cantilever-based nanosensors are exercised in the identification of comparably micromolecular compounds such as small-length nucleic acids and smaller pathogenic peptides or protein molecules. However, this highly in practice approach still faces certain challenges like differential immobilization chemistry and antibody affinity toward isomorphic antigens causing sensitivity issues (Saylan and Denizli 2020). Since the surface hydrophobicity and hydration sphere are important parameters for the determination of the epitomic region and immunogenicity for the generation of antibodies specificity, the magnitudes of measurement of such epidemic region in liquid are more crucial than the dehydrated conditions. Therefore, it becomes a vital task to maintain the character of the antibodies and their epitopes on the variable surfaces. The utilization of the professed “dip-and-dry” techniques is extensively applied in QCM and cantilever-based sensing platform. It implies that the antibody–antigen interaction is validated to ensue in a liquid environment, nevertheless, the measurements are estimated after the surface of the sensors is dried with nitrogen stream treatment. This step extendedly complicates the analysis pattern and therefore remains out of place and is incompatible with the advances of the new-age point of care (POC) device. In spite of this, in SPR-based sensors, the all-inclusive scrutinization is accomplished in a liquid environment, which makes SPR-based sensing application an advantageous characteristic for a POC sensor. In addition, the antibody–pathogen interaction occurs continually in dynamic mode in SPR assays. The continuity in the dynamics of antibody–antigen reaction allows nonspecific binding as the surface of the sensors does not allow the pathogen to settle over there compared to specific binding in the case of static-based assays. However, SPR-based approaches also have clear limitations in terms of sensitivity when compared to QCM-based and cantilever-based sensors (Lu and Kandlikar 2011).

3.2 DNA-Based Nanosensors

DNA-based biosensors are gaining popularity in the present scenario for detecting plant viral pathogens because of their possibility of detecting the genetic material of the viral strains with minimal quantity and with greater specificity at the molecular level. The DNA-based detection methods are now used globally for the identification of bacteria, viruses, fungus, protozoans, and other pathogens. Mostly single-stranded fragments of DNA are exploited as the molecular probes to bind with the pathogenic DNA and RNA on the detection surface, which may generate a specific signal in either colorimetric form or fluorescence energy transfer or other electrochemical-based signals. The major advantageous factor that contributes to the increasing demand for such detection platforms is the identification of the pathogen in the very early stage before the visualization of symptoms. Present-day technologies aid with the DNA/RNA extraction kits leading to total extraction procedure to few minutes and ease in DNA-sequencing techniques such as nanopore sequencing as well as the advancement in the hybridization techniques with isothermal amplification method present DNA as a versatile candidate for DNA based nanosensors for plant virus detection. Though DNA-based detection has variety of methods and assays but keeping account of the mode of transduction, four types of sensing applications are reported in the majority, they are electrochemical sensors, optical sensors, piezoelectric sensors, and DNA nanochips or arrays. The optical DNA-based nanobiosensors are further categorized into different sub-divisions like molecular beacons (MB), surface plasmon resonance (SPR), and quantum dots. The molecular beacons (MB) are based on a DNA probe that utilizes fluorescence for signaling. Surface plasmon resonance (SPR) uses energy from the incident light source on metal surfaces (usually gold films) that leads to the excitation of electrons (plasmons) generating an electric field. The immobilized probe molecule in the metal surface interacts with these plasmons and causes a change in the reflected angle which can be detected using SPR sensors (Nguyen et al. 2015). On the other hand, quantum dots (QD) are semiconductors that are nanocrystals and uses a definite wavelength of light for luminescence signals (Edmundson et al. 2014). A luminescence-based system is considered more efficient compared to fluorescence-based due to smaller emission spectra and greater photostability (Warad et al. 2004).

3.2.1 Molecular Beacons

Tyagi and Kramer introduced a novel nucleic acid detection technique and termed it molecular beacons (Tyagi and Kramer 1996). This process utilizes a specifically designed ssDNA with a stem-loop structural sequence. Customarily, the loop structure has the sequence of the DNA molecule, which is complementary to the target pathogenic DNA or RNA marker sequence. In addition, the stem region is custom synthesized to have 5′ end and 3′ end sequences that are complementary to each other. The 3′ end and 5′ end of the whole sequence hybridize to form the stem structure of the molecular beacon. The 5′ end is attached with a fluorophore molecule whereas the 3′ end is put together with the quencher molecule. The total assembly of the molecular beacon acquires a hairpin-like structure before hybridization with the target molecule. Hence the existence of the target nucleic acid in the sample is noticed by introducing a specifically designed molecular beacon that has the complementary sequence to target in the loop region. When the mixture of both the sample and the molecular beacon is set to thermal treatment from a higher temperature (80 °C) to a cooler temperature (20 °C), a typical fluorescence intensity is observed continuously during the whole process. The hybridization between the DNA molecule and the target molecule leads to the linearization of the hairpin-like structure causing the relatively higher intermolecular gap between the arm containing fluorophore and the other arm containing quencher molecule of the

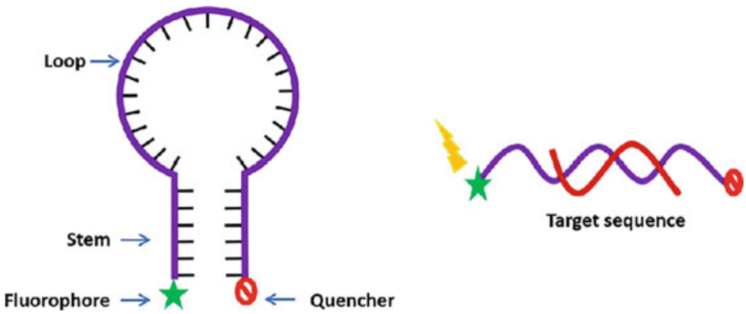

Fig. 4 Molecular beacons where the DNA fragment containing loop and stem linearizes when comes in contact with the complementary viral nucleic acid. When the target sequence available, the probe hybridizes and dislodges the quencher from the fluorophore resulting in fluorescence (Adapted from Wu et al. 2012)

molecular beacons. On the other hand, in the omission of any target molecule, the complementary sequences at 5′ and 3′ arms hybridize to form a stem-loop structure. It brings the proximity of the fluorophore with the quencher molecule. Therefore, fluorescence produced by the fluorophore is already quenched by the quencher molecule involving fluorescence resonance energy transfer (FRET). In cases where the target molecules are present, the loop structure with the complementary base pairs will hybridize with the target sequence. Such pairing is favored thermodynamically as the loop structure bears less free energy compared to other coiled or non-paired structures. As a result of hybridization between target and probe sequences, there would be a displacement of quencher from the fluorophore molecule. Hence, the fluorescence emitted by the fluorophore will not be able to transfer through the FRET process to the quencher molecule and the fluorescence signal will be uninterrupted. The whole set of machinery in the molecular beacons makes them a smart sensor candidate, which can detect the pathogenic DNA/RNA in a quantifiable way. The working of a molecular beacon is illustrated in Fig. 4. The molecular beacon-based probe has shown better detection on the basis of structural specificity and is therefore considered superior to other hybridization techniques. This technique is able to discriminate the target sequences even with the variation of one nucleotide (Navarro et al. 2015). Moreover, more than one molecular beacon can be possibly employed to detect several viral molecules in a single set of reactions. As an example, Eun and Wong (2000) developed two sets of molecular beacons for detecting plant viruses specifically the cymbidium mosaic virus (CymMV), belonging to the genus *Potexvirus*, and odontoglossum ringspot virus (ORSV), belonging to the genus *Tobamovirus* (Eun and Wong 2000). The first set of molecular beacons is able to detect the RNA-dependent RNA polymerase (RdRp) genes, whereas the other set can detect the coat protein (CP) genes of both CymMV and ORSV at the same time. These molecular beacons have the potential to identify multiple sets of viral strains by modifying the fluorophore and quencher arrangements. It is also required that the different fluorophores with different emitting ranges should not make interference with each other so that the recognition of different targets can be maintained. Since the genetic material of CymMV and ORSV is RNA, the first thing in the experimental procedure is to extract the RNA from the diseased leaves of the orchid plants. The collected RNA samples are further subjected to reverse transcription polymerase chain reaction (RT-PCR) with selected specifically designed primer sets. The amplified genome targets of the above-mentioned viral strains are then subjected to a molecular beacon-based hybridization assay. This is a successful method for detecting multiple virus gene targets in a single reaction mixture. In this particular context, the detection of plant viruses CymMV and OSRV is carried out with two different fluorophores. For detection of CymMV, the molecular beacon is specified by using fluorophore 6-carboxyfluorescein (FAM) whereas, for ORSV-specific molecular beacon, the fluorophore tetra-chloro-6-carboxyfluorescein (TET) is used. A compound named 6-carboxy-tetramethyl-rhodamine (TAMRA) is used as the universal quencher for these two fluorophores by binding at the 3′ ends of the molecular beacons (Eun and Wong 2000). Molecular beacon probes can be employed in nucleic acid sequence-based amplification (NASBA) technology to generate a rapid and sensitive fluorescent signal for the detection of apple stem pitting virus in apple trees (Klerks et al. 2001). NASBA is a technique that does not require thermal assembly since it can be handled at a constant temperature. The components of NASBA require three different enzymes, a molecular beacon, and two different primers for their functionality. This technique falls under the category of isothermal nucleic acid amplification method that amplifies plant virus RNA with the utilization of oligonucleotide primers and specific reverse transcriptase enzyme namely avian myeloblastosis virus-reverse transcriptase (AMV-RT), RNase H, along with the T7 RNA polymerase enzyme. The product of the NASBA that is the RNA amplicon is hybridized with the complementary sequence of the loop structure of a molecular beacon probe. This allows changes in the conformational arrangement of the molecular beacon leading to the dissociation of the fluorophore and the quencher. When this happens, using a suitable wavelength of light, the real-time intensity of the fluorescence signal confirms the presence of the viral amplicon. This methodology is also applied to detect sugarcane yellow leaf virus (Klerks et al. 2001). In another strategy, Lin et al. introduced an E-sensor for specific nucleic acid detection that can be applied in viral plant pathogen detection (Lin et al. 2014a, b). One more example of a molecular beacon probe-based nanosensor, the probe surface is attached to an electrode whereas the 3′ end of the loop structure of the probe is hybridized with DNA–biotin complex signal molecule. Then this signal molecule is labeled with streptavidin-horseradish peroxidase (SP-HRP) complex that specifically reacts with the biotin molecule to give an electrochemical response. Such electrochemical responses can be recorded and used as a strategy for detecting viral nucleic acids. Additionally, by means of complete mechanization of this recognition technique, the molecular beacon systems are capable of delivering a fast as well as precise nucleic acid-centered diagnosis method for examination of virus-free plant samples.

3.2.2 Aptamer-Based Plant Virus Detection

Aptamers are basically single-stranded oligonucleotides, which selectively bind to proteins and small molecules. These short oligonucleotides are very promising synthetic receptor molecules due to their advantage for in vitro selection and production. Aptamers are energy-stabilized structures that can hybridize with viral molecules strongly just like that of the antigen–antibody affinity. The aptamers-viral proteins or ligand interaction are advantageous and more preferable than that of antigen–antibody-based systems due to its stable structure, higher shelf-life, reusable, and capability of mass producibility (Tombelli et al. 2007). Owing to their advantageous sides aptamers are often considered as a fundamental unit of biosensors being the charge of a new dimension of biosensors called aptasensors, which includes only the functioning of aptamer-based biosensors. The sets of aptamer molecules are designated in vitro conditions depending upon their affinities for the particular ligand molecule. The target ligand molecule can be the whole cell organism like bacteria, viruses, or protozoans or can be a protein molecule or peptides. The selection of the aptamers is carried out using an enrichment method named selective evolution of ligands by exponential enrichment (SELEX). This method is employed to pin down the molecules with greater affinity from a pool of more than thousands (1015–1018) of randomly generated oligonucleotide libraries. Each oligonucleotide contains 20-80 random nucleotide regions located between two nucleotide primer binding regions in the gene. Several DNA and RNA aptamers with high affinity toward viral proteins or whole viruses have been successfully reported.

The first aptamers designed using SELEX are against the apple stem pitting virus (ASPV) whose coat protein is recognized by the aptamers on nanomolar scale (Balogh et al. 2010). ASPV belongs to the genus *Foveavirus* of the family *Betaflexiviridae* and is found in extremely widespread viruses of apple and pear trees globally. The nucleic acid material in such a virus is ssRNA and has more than nine thousand base pairs. It has five open reading frames (ORFs) encoding the antigenic viral coat proteins and other essential machinery for protein synthesis. ASPV attacks different apple and pear species and produces an eclectic ambit of symptoms varying from symptomless morphology to visible xylem pits in stem cells, epinasty, yellowing of veins, mottling of leaves, necrotic spot, or stony pits in fruits. There is a difference in the range of symptoms and effects and these variations depend on the kind of plant species, the cultivar variety, and the strain of the virus (Ma et al. 2019). The selection of aptamers is carried out by performing repeated cycles with the SELEX method. During the selection process, the DNA library containing the solution is incubated with a specific coat protein (like PSA-H or MT32 of apple and pears virus respectively) bound to nickel-nitrilotriacetic acid (Ni-NTA) agarose matrix that can purify protein carrying histone tagged through affinity chromatography (Balogh et al. 2010). The weakly bound or unbound DNA sequences are then discarded by the washing step. The proteins that are bound to the aptamers are eluted from the resin and used as templates in the PCR mixture. In the PCR, the amplification is carried out using unmodified forward and biotinylated reverse primers. The resulting PCR product is affirmed by gel electrophoresis, and incubated in a microtiter plate. Following incubation, the sequences not containing biotin are eluted. This solution is used in the next round of the SELEX process. The repetition of the SELEX cycles continues in the same way but the amount of protein is gradually reduced. To enhance the specificity of the selected aptamer sequences, counter-selection steps are introduced into the SELEX process following cycles 3, 6, and 9. The final cycle of PCR-SELEX involved a biotin-free reverse primer, which finally gives rise to the desired amplicon. The obtained PCR amplicons are further cloned (by inserting it into the p-GEM-T-easy vector by T/A cloning). Subsequently, the competent *E. coli* DH5α cells are transformed with the cloned PCR product using ligating solution mix. The aptamers molecules are then reorganized by the aligned application of the clone manager program. This purely aptamer-based method enables the exact determination of the coat protein concentration even in a complex matrix, containing bacterial proteins, and the detection method can be performed in a general laboratory facility. In a similar study, the significance of aptamers in coat proteins (PSA-H and MT32) for ASPV identification is explored along with enzyme-linked oligonucleotide assay (ELONA) followed with western blotting method (Komorowska et al. 2017). Another approach in which a direct, label-free detection of viral coat proteins (PSA-H and MT32) is carried out using surface plasmon resonance imaging biosensors as reported by Lautner et al. in 2010. In that investigation, thiol-labeled aptamers are adsorbed onto the gold SPR chips in the first step to bind with the antigens as the capturing agents. In the second step, the functionalized thiol derivative of tetra-methylene glycol is utilized to minimize nonspecific adsorption at the surface to reduce the signal/noise ratio. For practical purposes, aptamers for virus coat proteins (MT32 and PSA-H) of ASVP containing HS-$(CH_2)_6$-TTTT spacer are immobilized on gold-based surface plasmon resonance chips. Afterward, the identification of viral coat proteins in plant sap got examined on collected materials of the ASPV-positive plant. The presence of virus proteins could be confirmed by the magnitude of the SPR response in test samples in comparison to the control sample (Lautner et al. 2010). Such an aptamer-based method for testing plant viral proteins is a promising system for detecting viral pathogens. Considering one more example, the rice black-streaked dwarf virus (RBSDV) which infects many species from the Gramineae family that includes plants like rice, maize, wheat, and barley possesses a high threat for humankind as it causes severe loss of crop production. RBSDV belongs to the Reoviridae family and genus *Fijivirus* and known to cause rice black-streaked dwarf disease and maize rough dwarf disease (Eyvazi et al. 2021). RBSDV is a double-layered icosahedral virus. It contains 10 dsRNA segments (S1–S10) and six structural proteins (P1, P2, P3, P4, P8, and P10). Among these structural proteins, RBSDV P10 protein is the outer capsid protein that plays a significant role in RBSDV disease diagnosis (Wu et al. 2013). Diverse approaches have been documented for the diagnosis of RBSVD. Many contemporary methods like reverse transcription-polymerase chain reaction (RT-PCR), quantitative real-time polymerase chain reaction (qRT PCR), RT-loop-mediated isothermal DNA amplification (RT-LAMP), and blotting kits are incorporated in the virus diagnosis. However, an aptamer-based approach introduced

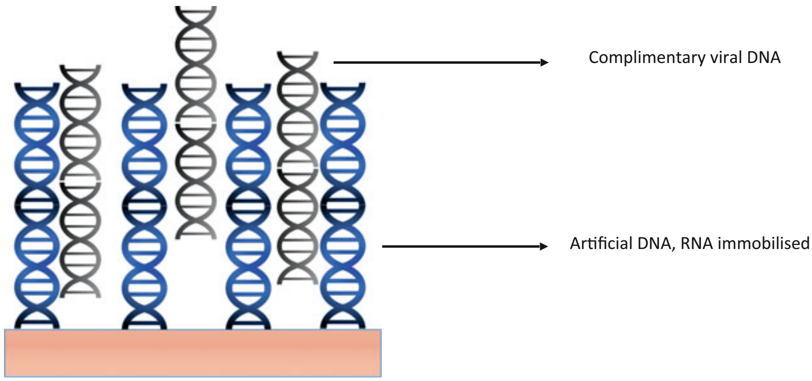

Fig. 5 An aptamer-based capturing mechanism where artificial DNA-based probes are immobilized which are allowed to bind with the antigen containing complimentary viral nucleic acid which hybridizes with the probes causing signal emission

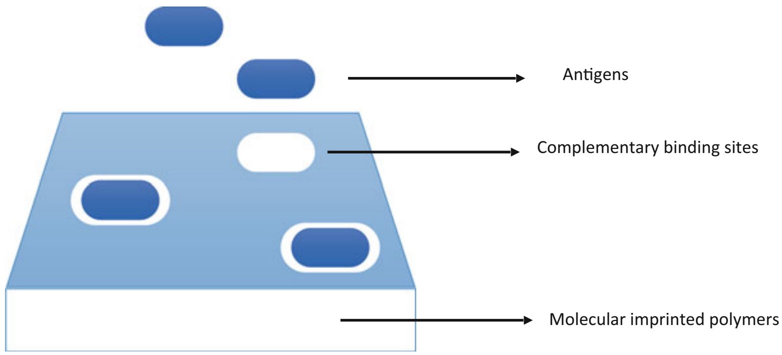

Fig. 6 The complementary binding site contains molecularly imprinted polymers that specifically bind to antigens (Adapted from Saylan et al. 2019)

by Liu and coworkers addressed the limitations of escalated costs of reagents and experimental setup in such methods (Liu et al. 2020).

Aptamers-based bionanosensors have shown more sensitivity and produced less background noise in the form of nonspecific binding in the field of immunohistochemistry. Moreover, various aptamer-based biosensors have been designed to use as lab-on-chip systems (Khan and Song 2020). Aptamer biosensors have advantages over antibody-based sensors in fewer variations, easy availability, and excellent diversity of recognition of ligand molecules. Although widespread use of aptamers in plant virus diagnosis is at its initial stages, the overall advantages will help aptamer-based nanobiosensors for getting more acceptance in virus–vector detection studies. Figure 5 depicts aptamer and Fig. 6 shows molecularly imprinted polymers that specifically bind to antigens.

3.3 Nanochips/Nanoarray

Constructed on an electronically confined surface, the nanochips are sets of arranged microarrays systems. These systems are composed of luminescence-founded oligo capture probes that are employed for the detection of hybridization. This nanotechnological intervention is extremely precise and combined with profound sensitivity to recognize the single nucleotide alteration happening in viral strains or isolates. The nanochips are designed to show a high sensitivity to discriminate between variations in a single nucleotide. In many crop viruses like Potato virus Y (PVY), potato virus X (PVX), and potato leaf roll virus (PLRV) in potatoes have been accurately identified by using nanochip-based techniques. In the administration of viral infections in agriculture, precautionary governance measure becomes competent only when the virus-free seeds or virus-free seedlings are made available to the farmers. Consequently, a rapid, precise, combined with applicable analysis of plant viral strains is of imperative importance. In this view, the detections established on visible signs are not exclusively applicable, while these symptoms also can stand concomitant with nutritional insufficiencies along with interactions linking crop plants and viral diseases. Nanodiagnostic kits will go a long way in reducing the burden of non-detection of viral diseases in agricultural plants. Future research is carried out to unravel new methods or to optimize the existing kits for plant virus detection with minimum false signals. Also, the advantage of such kits or methods depends on the capability of detecting the host plant samples infected with a very low concentration of virus. Microarray or chips-based detection system employs high throughput screening systems and such systems are useful in the broad-spectrum identification of plant virus (Sosnowski et al. 1997; López et al. 2008). However, the implementation of this technology has been constrained to some factors also, but still, its application in the field of viral detection is well recognized. The nanochips-based approach has been utilized in the identification and recognition of different potato viruses and tobamoviruses (Pallás et al. 2018). In other studies, the oligonucleotide-based microarray is used to evaluate the viruses in fruit tree plants and assess its efficacy in detecting viruses (Lenz et al. 2008). Zhang and coworkers prepared a microarray-based detection system with a limited number of probes for detecting a diverse group of banana viruses. Their group used the reverse transcription loop-mediated isothermal amplification (RT-LAMP) method for designing such a microarray-based detection system. For every detection system, the cost, ease of function, and complexity are major hindrances in the proper implementation of molecular techniques for viral recognition. The paradigm shifts toward the next-generation sequencing techniques like nanopore sequencing and other methods like isothermal amplification and quantum dot-based direct detections are gaining more popularity than this technique (Zhang et al. 2018). Similarly, peptide-based nanosensors are also being developed to act in the present scenario. Even though limited investigative nano-chip-based approaches have been reported intended for the recognition of crop viruses, the issue appears probably that the impending advantages of equivalent breakthroughs will hustle auxiliary advancements. Nevertheless, there are a certain number of unforeseen challenges to remain surmounted prior to the extensive application in a diagnosis sensor. One of the challenges is the designing of an appropriate oligonucleotide probe, which has a tendency to acquire secondary structure when bound to the solid surface. Such probes will not behave according to their design. The second major issue is regarding the sensitivity as these assays are not label free and hence have a sensitivity issue. Nonspecific labeling techniques take more time to hybridize completely around an overnight's time. Chip-based methods grounded on glass slide platforms are correspondingly not apt for high throughput testing. Additionally, they need a large amount of manual manipulation to complete the technique effectively.

3.4 Peptide-Based Sensors

In recent times, peptides provide possible and new avenues in building dynamic supramolecular flexible structures. Attributed to their adaptive physiochemical characteristics properties, these specific oligopeptides are capable of folding themselves in compact and condensed structural motifs resulting in nanosized architectures. These nanosized structures can take various spatial arrangements like monolayer or bilayer fibers, tubular structures, flat strip-like surfaces, and circular micelles. A particular oligopeptide-based nanostructure and its self-assembly are determined on the basis of its weaker noncovalent intermolecular interactions. Such weak interactions exhibited by side chains of amino acids like electrostatic attraction or repulsion, aromatic p-stacking by aromatic amino acids, hydrogen bonding, hydrophilic, hydrophobic, and Van der Waals forces play a crucial role with target molecules during molecular recognition. Short oligopeptides that are synthetically synthesized can substitute many natural existing proteins and perform better in recognizing molecules due to a higher degree of rotation around the peptide bonds. The 20 different naturally occurring amino acids are associated with the formation of oligopeptide assemblies. These assemblies distinguished by the amino acids side chains at the central carbon position add to the structural variability and hence the recognition capability. Such oligopeptides with variable R-group containing carboxyl groups (COO·) or protonated amine groups ($NH3^+$) show ionic characteristic, which helps in bonding with ligand molecules. This zwitterionic nature is oligopeptides that provide a different level of binding specificity with the molecules of interest. The negatively charged carboxyl group and the positively charged amine group comfortably form a layer of hydration using hydrogen bonding on the surface of the sensor. Due to the presence of ionic charges on amino acids, there are hydrophilic and hydrophobic regions over the surface which changes the adsorption capability of such oligopeptide nanostructures. If the overall charge on the oligopeptide structure remains neutral then there is no adsorption of ligand molecule compared to charged oligopeptides. Presently, peptide science and specific oligopeptide structures are gaining attention owing to their simpler process of synthesis. Such synthetic oligopeptides have been exploited in the field of nanosensors as they can identify ligands on the basis of higher affinity, higher sensitivity, adaptability, versatility, and chemical diversity. It is perceived that synthetic oligopeptides serve better conformational and structural integrity compared to many proteins. Moreover, modified oligopeptides can be designed with a greater affinity to the target molecules like coat proteins. This oligopeptide sequence utilizes specific enzymatic substrates or inhibitors for screening and conjugating reactions. Attributed to these particular properties, oligopeptides serve as a possible biosensor material that can be developed to bind ligands with higher sensitivity. One of the simpler methods of making an oligopeptide-based biosensor is to conjugate a synthetic oligopeptide of interest with either signal markers or signal amplifiers. Such biobased structures can be customized into large-scale production and commercialized for wide-scale applications including in detecting viral signals. The application of oligopeptide-based biosensors is already known in many fields of diagnostic sciences like health diagnostics, clinical testings, biohazard testing, molecule-like pesticides identification, environmental signaling, and agriculture fields. In crop biology, one of the utilities of oligopeptide-based biosensors is in detecting crop viruses rapidly with higher accuracy. The major reason cited for such identification is due to the higher sensitivity even with the permission level of torsion flexibility in the oligopeptide structures. Many sensor platforms are developed where the oligopeptides and the ligand molecule can be detected effectively. Some of them are quartz-based crystals, SPRs, voltammeter, sound waves-based, and amperometric-based sensor systems (Shumeiko et al. 2021). The working principle of an oligopeptide-based biosensor involves an oligopeptide of interest labeled with a detector molecule or a redox connector system that is etched onto a metal-based electrode surface that uses certainly suitable compound that enables immobilization of oligopeptide on the surface. In addition to this, a spacer molecule is often included, which allows better accessibility of the analyte with the oligopeptide for a higher probability of interaction (Hao et al. 2020).

Oligopeptide-based molecular beacons also exist which contain a similar structure to that of the DNA-based molecular beacons consisting of the fluorophore and quencher pairs but in this case, the oligopeptides show conformational alteration upon binding to the target molecule. The shifting conformation of the target-bound oligopeptide induces changes in the spectral properties of the fluorophore that is attached to it. Thus, the alteration in the spectral properties that implies the altered distance between the probe-quencher pair could be monitored by the FRET mechanism. Such oligopeptide beacons are reported for the detection of human-affecting viruses but to date plant virus detection has yet to be established. The structure of peptide-based biosensors can be categorized according to the mode of its detection and structural operations or application. For the detection of target molecules including plant viruses, such nano biosensors either use these oligopeptides in generating electrochemical or electroluminescence signals. Additionally, some of the analytical aspects of these methods are also required in sensor systems like the range of detection, the possibility of several reiterations of testing, and sturdiness even in adverse climatic situations. Electrochemical biosensors provide an alternative to a molecular-based diagnosis system in which screen-printed electrodes and oligopeptides provide a better detection system (He et al. 2021). The employment of an efficient electronic surface marker like quartz crystal microbalance or a cantilever or graphene sheet for the detection of electron transfer processes happening between the oligopeptide and its target analyte is necessary for the development of the oligopeptide-based electrochemical sensor. The transfer of ions or electrons from such electronic surface markers onto the electrode is highly governed by the association between the oligopeptide and the target analyte. Among various analyte biomolecules, oligopeptides remain crucial for the recognition of proteases and kinases through functioning them as substrates and have been extensively explored for the development of protease or kinase sensors. Protease enzymes exist under the category of hydrolases enzymes that can hydrolysis the oligopeptide bonds in a protein to carry out degradation of proteins or proteolysis. Serum proteases are quite unanimous in every living organism. However, the viral pathogens invade the host machinery by viral proteases like TEV protease, which are recognized by having a long carboxyl-end tail. Enzymes like TEV protease shield the analyte molecule to build a fastening channel. Such fastening channels are formed around the analyte with the binding of enzymes and such interactions are mediated by the side chain specificity. Protease-recognizing oligopeptide sequences take part a vital part in the building of novel biobased sensors. These oligopeptide sequences can be excised with fine precision combined with competence by the protease enzyme at specific locations on the sequences of the oligopeptide. This reaction of excision mechanism or the information regarding the electron/analyte transfer can be efficiently conveyed through the difference in the behavior of signal surface markers attached to the viral protease-specific oligopeptide sequence. Because of its high specificity toward analytes, the TEV is highly exploited as a biochemical tool for detection.

Oligopeptide-based affinity tags are also taken into use for the production of recombinant proteins and their purification. These recombinant oligopeptides are further followed by a viral protease identifying sequence for the removal of such affinity tags. For example, a rat monoclonal antibody 2H5 has been constructed which contains a recognition sequence for Tobacco Etch Virus (TEV) protease and is reported by Brungardt and group (Brungardt et al. 2020). In the crystal structure of the 2H5-TEV complex, it reveals the α-helical conformation in the binding groove of long TEV peptides having water-soluble ends. This peptide (2H5-TEV) is tagged with another peptide named PA making it a double-tagged complex (2H5-TEV-PA) and is patented by the research group for the development of recombinant protein purification tool (Tabata et al. 2018). The PA tag that is a 12 amino acid long peptide can bind strongly to antibody (anti: PA) molecules attached to a solid surface, to aid in the construction of biosensors. However, this oligopeptide tagged with another peptide also can act as a detecting candidate or capturing agent for recognition of the TEV protease. When this double tag complex (2H5-TEV-PA-anti: PA) is attached to specific proteins of interest, it is confirmed to have two epitopes that can bind two antibodies and get detected by sandwich ELISA assay (Tabata et al. 2018). However, the TEV protease enzyme is also a pathogenicity determinant in the members of the family Solanaceae. This TEV viral isolate is a member of the potyvirus group that mainly spread diseases to several species of plants belonging to the Solanaceae family. Agricultural crops including several species of capsicum, tomato (*Lycopersicon esculentum*), and tobacco (*Nicotiana spp*.) are affected by this TEV virus. Oligopeptide-based nanosensors have been promising at a precipitous pace predominantly in the timeline of the last decade. These new-age sensors have presented the countless potential to be applied in agricultural fields. Rapid approachable, easy to handle and access to such oligopeptide-based nanochips will definitely go to connect with the upcoming breakthrough in detecting agricultural crop pathogens.

3.5 Future Point of Care Devices Assembled on Biomolecules with Nanosensor Systems

Detection, identification, and quantification at the very initial stage are crucial in plant viral disease management and breaking the epidemic chain. Identification of inoculum in point of care (POC) devices and high multiplex detecting capability are the most important aspects. The superlative qualities of these detection assays demand ultra-high specificity to work in precision, superior sensitivity, reproducibility, rapid response, economic and cost-effective combined with high throughput detection. The benefit of POC diagnostic devices is that it provides quick and accurate results in situ. Such a diagnostic kit will be also helpful in providing information regarding the plant virus disease. It is an asset for many plant growers and helps them to make proper decisions regarding pest or pathogen control and improve crop productivity. The implementation of such tiny miniaturization of lab on a chip device also saves the concurrent labor charges related to sample transportation to centralized labs from farmlands. Such devices also help to reduce the cost of transportation and handling of the samples to the laboratories and thus reduce the risk of mishandling, contamination, and loss of valuable time. POC diagnostic kits should be handy as well as user affable so that a farmer with no scientific temper can able to handle them and operate them without any error. The vast majority of current applications of POC devices depend on the technology that is based on PCR or RT-PCR. Another approach used apart from PCR based is the isothermal technique in POC devices that is as effective in detection as the PCR-based assays (Baldi and La Porta 2020). Isothermal techniques or based POC systems are able to participate in processes where there is no need for temperature variation. The devices based on this system perform at constant temperature and that is an advantageous system for the development of biobased nanodevices. The technique of isothermal amplification is quite parallel to the processes of the conventional PCR steps. However, the denaturation step that requires heat for the separation of the two strands of the double-helix DNA is not needed in the isothermal amplification process. It is also a matter of concern that the genre of the viral pathogen, the kind of crop under the monitor, and the technological competency of that region play role in the suitability of adopting the kind of technology, isothermal or nonisothermal based. One of the isothermal techniques that can be used for viral pathogen detection is loop-mediated isothermal amplification (LAMP). It is a nucleic acid-based amplification assay reported in the year 2000, which has gained immense popularity and wide application due to high detecting efficiency, better specificity, simplicity in mechanism, and rapid response (Notomi et al. 2015). LAMP uses four unique primers that identify six specific regions on the target DNA sample molecule. Out of four unique primers, two are called inner primers and two are called outer primers. Inner primers contain coding and non-coding sequences that hybridize and initiate DNA replication. The outer primers then separate the double-stranded DNA into a single strand, which folds into a loop-like structure at both ends. Finally, this loop structure of DNA undergoes a repetitive cycling reaction and accumulates dumbbell-shaped products with repeated sequences of target DNA. This dumbbell-shaped DNA can be conjugated with markers for the detection of viral nucleic acids (Lau and Botella 2017). Similar to the LAMP technique, reverse transcriptase-loop-mediated isothermal amplification (RT-LAMP) works on RNA rather than DNA. In this, the RNA is first made into cDNA using reverse transcriptase and then the cDNA is amplified using the LAMP method. Loop-mediated isothermal amplification (LAMP) is considered one of the best systems for the development of an amplified product, which in turn increases the detection sensitivity (Lau and Botella 2017).

Helicase-dependent amplification (HDA) is another substituent isothermal method advanced by New England Biolabs in 2004 (Nguyen et al. 2015). In this process, DNA helicase plays an important role in the separation of double-stranded DNA to single-strand DNA under uniform temperature conditions (Lau and Botella 2017). Once DNA strands are separated, single-stranded binding proteins (SSB) and MutL endonuclease bind to ssDNA and prevent them from reannealing. Helicase-dependent amplification can take up to an hour to form a detectable amount of PCR amplicons, which can be easily analyzed. This method is also similar to the normal PCR but differs in the aspect of simpler steps and the nonrequirement of multiple temperature cycling steps. For an instance, Wu and their group developed a method for detecting tomato spotted wilt virus by reverse transcription thermostable helicase-dependent DNA amplification (Wu et al. 2016).

Another variation of HDA is recombinase polymerase amplification (RPA), which denatures the DNA without using any heat. This method relies on enzymes to denature the dsDNA followed by primer binding to the target sequences. Once the dsDNA is denatured, the recombinase enzyme binds to the primer at specific target sequences and then anneals. Once the primer annealing step takes place, the recombinase enzyme dissociates from the primers, and DNA polymerase enzymes bind to those sites to initiate the normal replication process and amplify the DNA fragments. A D-loop is created which is attached with SSB proteins for stability whereas the DNA polymerase continues to make amplification and overall this technique is getting popularity in nanodiagnostic due to its heat independent process (Lillis et al. 2016). Recombinase polymerase amplification (RPA) is also used in the development of the technique for the detection of viruses in crop plants like banana bunchy top virus, bean golden yellow mosaic virus, tomato mottle virus, tomato yellow leaf curl virus as well as containing RNA genome containing plant virus-like little cherry virus 2, plum pox virus, and rose rosette virus (Babu et al. 2016). Nowadays, next-generation sequencing (NGS) technologies have shown a future in the space of diagnostic science because of their high potential. This NGS technology can identify multiple virus strains in a single experimental setup without any previous information on viruses (Withers et al. 2016; Rott et al. 2017). It is still a challenge in utilizing NGS in building POC as the NGS approach is expensive, needs sophisticated instrumentation, and has several steps in preparation and analysis. On the other hand, POC should be rapid, sensitive, and easy to operate.

Isothermal-based or antibody-based diagnostic methods are clearly faster and superior to the traditional detection techniques. Sometimes, the specificity of such detection approaches is questioned citing the cross-reaction with other viruses resulting in mistaken plant viral pathogen identification (Lau and Botella 2017). Another factor that limits the use of such methods is the short shelf lif**e** (Murphy et al. 2012). DNA-based techniques for viral pathogen identification need certain factors for improvement like the apparatus needed to be worked continuously or under changing temperature and for this continuous power supply is needed to become a POC for field application. (Sint et al. 2012). Such limitations can be addressed by using systems like isothermal amplification that increase the capability of POC applications. Such a system can work independently or can be coupled with other systems like the rapid readout method to analyze amplified DNA products. Table 1 provides a list of rapid detection methods designed and implemented in the detection of crop viruses in recent years. Nowadays, there is an urgent need and demand from farmer's communities throughout the globe for portable sensor devices that can be easily handled, need minimum training to operate, and broad-spectrum range for better dissemination of pathogen detection and diagnosis on agriculture products. This might bring prodigious welfare to agriculture globally, and it will help in controlling the epidemic causing viruses to a better extent. It also helps in the monitoring of the large agriculture field areas and detects viruses before the disease symptoms are observed. On similar grounds, it will be easier to check the exotic or imported crops or crop products for a viral infection that can cause serious crop loss, once amalgamated with locally grown agriculture products. Apart from quarantining foreign agricultural products, a pathogen monitoring system at the forest level, environmental level, or medical level will always help in providing early signals for immediate remedial.

4 Conclusion

Detection of disease-causing virus and its diagnosis is requisite in almost every crop disease management program. Early detection and identification of signals or symptoms will always be helpful in this regard. Detecting the virus in the air, water, or in-plant samples will help to limit the damage and prevent it from getting into an epidemic. A timely intervention in detecting viruses allows the application of control strategies and protects the crop plants and thus farmers from productivity loss.

Table 1 Selected list of detection methods used in the field of crop plants to detect virally transmitted diseases

Sl. no.	Viral strains	Capturing mechanism	Detection methods	References
1	Citrus tristeza virus in crude plant sap	Polyclonal antibody	Lateral flow immune assay	Maheshwari et al. (2017)
2	Yam mosaic virus (YMV) and yam mild mosaic virus (YMMV)	RT-RPA (isothermal-based RT-RPA Assay)	Fluorescence (20 min) confirmed with multiplex PCR	Silva et al. (2018)
3	Rose rosette virus (plant extract)	RT-RPA	Colorimeter and multiplex PCR	Babu et al. (2016)
4	Cucumber green mottle mosaic virus (CGMMV)	RPA	Fluorescence and PCR (30 min)	Jiao et al. (2019)
5	Watermelon mosaic virus (WMV), zucchini yellow mosaic virus (ZYMV), and papaya ring spot virus (PRSV-W)	RPA	Fluorescence and nested T PCR	Rajbanshi and Ali (2019)
6	Cherry virus A (CVA), cherry necrotic rusty mottle virus (CNRMV), little cherry virus-1 (LChV-1), and prunus necrotic ringspot virus (PNRSV)	RNA	Multiplex RT-PCR	Noorani et al. (2013)
7	Grapevine leafroll-associated virus type-3 (GLRaV-3)	RT-LAMP	PCR and colorimetric	Walsh and Pietersen (2013)
8	Plum pox virus (PPV)	RT-RPA	LFA -fluorescence	Zhang et al. (2014)
9	Ginger chlorotic fleck-associated virus-1 and 2 (GCFaV-1 and GCFaV-2)	RT-LAMP, RT-RPA	Colorimetric	Bhat et al. (2020)
10	Banana bract mosaic virus (BBrMV)	Anti-BBrMVCP immunoglobulins (IgG) embedded with Au-NPs	Lateral flow immunoassay (LFIA)	Selvarajan et al. (2020)
11	Bean golden yellow mosaic virus (BGYMV), tomato mottle virus (TMV), and tomato yellow leaf curl virus (TYLCV)	RPA	Heating at 37 °C followed by PCR	Londoño et al. (2016)
12	Tomato chlorotic dwarf viroid (TCDV)	RT-RPA	RPA assay and RT-PCR	Hammond and Zhang (2016)
13	Banana bunchy top virus	RPA	Isothermal amplification	Kapoor et al. (2017)
14	Apple rubbery virus 1 and 2	Illumina sequencing	High throughput sequencing of dsRNA	Rott et al. (2018)

(continued)

Table 1 (continued)

Sl. no.	Viral strains	Capturing mechanism	Detection methods	References
15	Blackberry leaf mottle associated virus (BLMA)	Illumina sequencing	High throughput sequencing of dsRNA	Hassan et al. (2017)
16	Citrus chlorotic dwarf associated virus	Illumina sequencing	High throughput sequencing of small RNA	Loconsole et al. (2012)
17	Citrus tristeza virus	Carbon nanoparticles quenchers with CdTe quantum dot labeled antibodies	Fluorometric immunoassay	Shojaei et al. (2016a, b)
18	Yam mosaic virus	CT-RT-LAMP	Isothermal amplification and chromogenic detection	Nkere et al. (2018)
19	Grapevine red blotch virus	RPA	Isothermal amplification	Li et al. (2017)
20	Citrus leaf blotch virus (kiwifruit)	RT-LAMP	Isothermal amplification conjugated with the lateral flow dipstick	Peng et al. (2021)
21	Chilli veinal mottle virus (ChiVMV)	RPA	Isothermal amplification	Jiao et al. (2020)
22	Rice stripe virus (RSV)	Polyclonal antibody	Dot blot and ELISA	Zhang et al. (2021)

Hence, timely detection of viruses in the field will always remain crucial and therefore novel strategies are tested and routinely investigated to find suitable methods of diagnosis and detection. Such novel strategies or testing materials detect viruses nucleic acid or protein must detect rapidly, should be easy to work at and have on-field applicability. Nanotechnology is a futuristic science and many recent developments using this science show promising results in early pathogen detection and diagnosis. Current technology like SPR, QCM, cantilevers, molecular beacons, aptamers, and organic molecules-based nanosensors, all can be refined further and have the potential to become futuristic sensor devices for virus detection. Many challenges do coexist with such state-of-the-art nanoappliances like making better designs, keeping low cost, nullifying false results, better specificity, and stability. Another matter of concern is the operation of such devices under variable climatic conditions, differential temperature, and humidity. In this regard, antibodies or nucleic acid-based POCs can serve as a suitable material for their robustness and conformational flexibility that can maintain sensitivity even in an unstable environment. Specifically, better amplification apparatuses and high throughput sequencing systems make nucleic acid, a molecule for future material for nanosensors. Present knowledge leads to custom-designed oligonucleotides that can fold into three-dimensional structures and can be easily amalgamated with nanobiosensors. In the future, such biomolecules integrated nanostructures can help farmers and thus increase the agricultural productivity of a nation by reducing the burden of pathogen-based crop loss.

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Polymeric Nanocomposites-Based Agricultural Delivery: Recent Developments, Challenges, and Perspectives

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1 Introduction

Agribusiness is in every case a generally significant and stable area as it creates and provides crude materials to food and feed ventures. The restriction of normal assets (production land, water, soil, etc.) and the development of the populace on the planet guarantee horticultural improvement to be increased the economy in a sustained way (Nair et al. 2010). This adjustment will be essential for accomplishing numerous elements in a upcoming years. Farming supplement offsets contrast discernibly with monetary development, and particularly from this gathering, the improvement of the soil's fruitfulness increased a lot in non-industrial nations (Yan and Chen 2019). The advancement of farming is quite necessary for the global crop production and sustainable devleopment of world. Thus, we need to make one striking stride for agribusiness advancement. In this world there are groups of people who are below destitution level and who are being scattered in the country region where farming augmentation has not been viable (Capaldi Arruda et al. 2015). In this way, new innovation needs to be received that distinctly centers around improving rural production. As of late, food and dietary security are completely deliver into the new information. Horticultural improvement additionally relies upon social considerations, wellbeing, environmental changes, energy, biological system measures, common assets, matchless quality, etc., and should likewise be reported in explicitly objective arranged purposes (Dietz and Herth 2011; Aslani et al. 2014). Farming sets out a course for recuperation; accordingly, the natural execution is required and simultaneous investment of evolved lifestyle environments are needed comparable

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with rural food production. Almost certainly the manageable development of horticulture absolutely relies upon new and imaginative methods such as nanotechnology (Wang et al. 2016). We would like to go back to Feynman's talk in 1959 on "A lot of room at the base," in which he said that from this very day, the nano-measure is in progress. Thereafter, nanotechnology grows clearer, because later instruments were created to consider or confine nanomaterials (NMs) in a precise manner. Moreover, the quantity of distributions identified with the term of "nano" was likewise developed dramatically. In 2016, in excess of 14,000 reports of nanotechnology in food or farming were recorded (Sharifi et al. 2012). Likewise, in excess of 2700 licenses coordinated with these rules are found in a world patent data set. The world market size of nanotechnology in 2002 was about US$ 110 billion and was anticipated to develop to US$ 890 billion from 2015 as per the Helmut Kaiser Consultancy. The improvements in nanotechnology in materials and hardware have higher elements than other applications (Mortezaee et al. 2019). As of late, food and horticulture additionally require a high measure of NMs, particularly in bundling. The North American Free Trade Agreement area shares the greatest cut of the market size; however, Europe and Asia, particularly China, Japan, and India likewise have progressed (Hong et al. 2015).

2 Advent of Contrived Nanomaterials

Nanomaterials have attracted extraordinary interest, particularly in the field of horticulture, which has increased the profitability of harvests with less expense and waste. NMs offer economic adequacy in the field of horticulture, including assurance and production of harvests. Huge headway and improvement of the newer farming innovations are urgently required owing to consistently expanding food requirements universally. Worldwide food production should be expanded around 70–100% by 2050 to fulfil the needs of the developing populace. In this unique situation, agribusiness made various creative advances such as half and half species, combination synthetic compounds, and biotechnological improvements (Melegari et al. 2013; Kirchner et al. 2005). In any case, the persistent production of farming yields may be one of the greatest difficulties because of the absence of supplements/changes in the environment. To conquer such issues related to the deficiency of production or improvement in the yield of harvests, ranchers persistently utilized agrochemicals. Unreasonable utilization of these agrochemicals prompts the decay of soil, the debasement of agro-biological systems, and ecological issues. In this unique circumstance, NMs have made mechanical headway, may be changed and associated with areas that give more current rural apparatuses to the administration of stresses (biotic and abiotic), discovery of diseases, improved supplements of retention capacity, and movement capacity (Li et al. 2008). Then again, NMs may assist with understanding horticultural science just as a connection of NMs with plants, upgrading the healthy benefit as well as the profitability of the harvests accordingly. Nonetheless, the specific job of NMs in agribusiness remains a worry. Various NMs, including carbon-based NMs (single-walled carbon nanotubes [SW-CNTs], multi-walled carbon nanotubes [MW-CNTs], carbon nanofibers [CNFs], graphene and fullerenes, metal and its oxide-based NMs, polarized iron [Fe] nanoparticles (NPs), aluminum oxide [Al_2O_3], copper [Cu], gold [Au], silver [Ag], silica [Si], zinc [Zn] NPs and zinc oxide [ZnO], titanium dioxide [TiO_2], and cerium oxide [Ce_2O_3], etc.) and bio-composite NMs have been created (Abdal Dayem et al. 2017a; Stone et al. 2007; Karimi et al. 2018; Srivastava and Majumder 2008). These NMs are effectively utilized in the field of horticulture for production and assurance of yields. In any case, phytotoxicity, the debasement of soil, huge scope creation, agglomeration, and a successful conveyance framework are other concerns. Then again, CNFs have the expected capacity to convey micronutrients in plants (Cu/Zn NPs) in a controlled way. Notwithstanding, CNFs likewise require a polymeric conveyance framework for genuine applications (Li et al. 2013). In this specific situation, polymeric nanocomposites have become quite possibly the most encouraging instruments for the conveyance of micronutrients and agrochemicals in the plant framework. A few polymers, for example, polyvinyl acetate (PVA), chitosan, polyvinyl-pyrrolidone (PVP), starch, hyaluronic acid (HA), poly(lactic-co-glycolic acid) (PLGA), poly-lactic acid (PLA), etc., have been utilized as transporters for the conveyance framework of different natural applications because of their high biocompatibility, biodegradability, nontoxicity, cost adequacy, and fantastic film-shaping capacity (Oehme and Wolfbeis 1997; Verma and Singh 2006; Han et al. 2001). Different cycles, for example, cross-connecting, emulsion development, and self-gathering have been utilized for the amalgamation of polymeric nanocomposites that work with the controlled arrival of agrochemical/micronutrients inside the plants. The exemplification of NMs by utilizing polymeric lattice likewise supported benefits to improve the adequacy of the NMs, diminishing cell harmfulness and ecological pollution. Then again, potent polymeric materials and conveyance framework have the likely capacity to convey the qualities/biomolecules/micronutrients inside the plants and furthermore ensure infections and microbes (Aruoja et al. 2009). This book section centers around the different NMs and polymeric composites that expand the plant development and collaboration of NMs with plants, qualities/biomolecules/micronutrient conveyance, and discusses the headway made by hereditary designing utilizing NMs.

Nanotechnology can play a significant part in efficiency through the control of supplements too, as it can also partake in the observation of water quality and pesticides to support the advancement of horticulture (Buledi et al. 2020). NMs have such different resources and exercises that it is difficult to convey an overall appraisal of their wellbeing and ecological dangers. Properties (other than the size) of NPs have an effect on toxicity incorporating compound synthesis, shape, surface construction, surface charge, conduct, total molecules (amassing) or disaggregation, , etc., and may connect with the designed NPs. Thus, even NMs of a very synthetic arrangement that have various sizes or shapes can show their diverse toxicities (Borah et al. 2015). The ramifications of nanotechnology research in rural areas has become vital, even a key factor for reasonable turns of events. In the agri-food zones the relevant uses of nanotubes, fullerenes, biosensors, controlled conveyance frameworks, nanofiltration, etc., were noticed. This innovation ended up being a great asset to the management of farming fields, drug conveyance components in plants, and assists with maintaining soil richness. Additionally, it is in effect likewise assessed consistently in the utilization of biomass and horticultural waste, in the food handling and food bundling framework, as well as hazard evaluation (Ravi et al. 2013). As of late, nanosensors have been broadly applied in the agribusiness because of their qualities and speed for ecological observation of defilement in the soil and in the water. A few sensors dependent on nano-identification innovation, for example, biosensors, electrochemical sensors, optical sensors, and gadgets, will be the principle instruments for identifying the substantial metals in the following range. NMs not only straightforwardly catalyze corruption of waste and poisonous materials but it also helps to improve the productivity of microorganisms in the debasement of waste and harmful materials. Bioremediation utilizes living organic entities to separate or eliminate poisons and damaging substances from farming soil and water (Dwivedi et al. 2015). Specifically, some different terms are also commonly utilized such as bioremediation (useful microorganisms), phytoremediation (plants), and mycoremediation (growths and fungi). Consequently, with bioremediation the heavy metals can be removed from the soil and water ecologically and effectively using microorganisms. Subsequently, the agrarian bioremediation helps in manageable remediation advances to determine and reestablish the usual state of the soil. It is a fascinating to consider that the nano–nano collaboration eliminates the poisonous segment of the rural soil and makes it satisfactory (Musarrat et al. 2010).

3 Types of Nanomaterials and Their Functionalities

The various types of agro-based NMs and their functionalities are categorized as follows (Fig. 1):

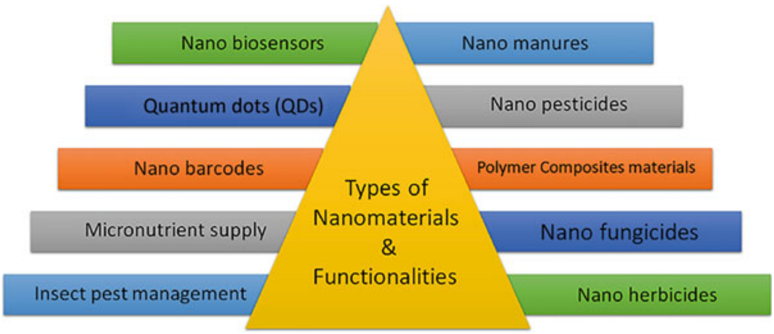

Fig. 1 Schematic representation of various types of nanomaterials and their functionalities

3.1 Nano Manures

In the new decade, nanofertilizers are unreservedly accessible, and yet rural composts in particular are as yet not formed by significant synthetic organizations. Nanofertilizers may contain nano zinc, silica, iron, and titanium dioxide, ZnCdSe/ZnS center-shell quantum dots (QDs), InP/ZnS center-shell QDs, Mn/ZnSe QDs, gold nanorods, center-shell QDs, etc., and should underwrite control of delivery and improve quality. Investigations of the take-up, natural destiny, and harmfulness of a few metal oxide NPs, such as Al_2O_3, TiO_2, CeO_2, FeO, and ZnONPs, were carried out seriously in the current decade for farming production (Patterson 1939; Wahab et al. 2014; Hunter and Kuykendall 2007; Hunter et al. 2007). Some of the most common and highly potent nanofertilizers are listed and elaborated in Table 1. The inadequacy of zinc has been archived as one of the principle issues in restricting farming profitability and in the fertility of soil. Metal oxide NPs are radiolabeled by direct proton assault or improved during combination with ^{18}O to produce ^{18}F (Lloyd-Jones et al. 2006). Size, level of collection and zeta capability of the metal oxide NPs are concentrated within the sight of proteins and cell media. Besides, NP take-up and intracellular destiny are trailed by particle bar microscopy, transmission electron microscopy, Raman compound imaging spectroscopy, and confocal laser examining microscopy. Later on, a supportable bio-based economy that utilizes eco-effective bio-measures and sustainable bio-assets will continue to decline and substitute the damaging materials in setting up applications, and in this way it will assume a significant part (the vital test) in the improvement of the innovations needed to deliver to the twenty-first century (Binaeian et al. 2012). The amassing of information in the fields of environment, science, biodiversity, material science,

Table 1 List of some commercial nano fertilizers worldwide

S. No.	Products	Ingredients	Manufacturer Company
1	NANO GREEN	Grain, soybean, potatoes, palm, and coconut extract	Nano Green Science, India
2	TAG NANO	Vitamins, probiotics, humic acid, and chelation of micronutrients with protein-lacto-gluconate	Tropical Agro system India Pvt Ltd
3	Nano-Gro	Immunity enhancer and plant growth regulator	Agro Nanotechnology Corporations, USA
4	Nano Max NPK Fertilizer	Organic acids chelated with micro and macro nutrients, amino acids, vitamins, probiotics, and carbon	JU Agri Sciences Pvt Ltd., New Delhi, India
5	Biozar Nano Fertilizers	Composites of micronutrients, macronutrients, and organic compounds	Fanavar Nano Pazhoohesh Markazi Company, Iran
6	Master nano Chitosan Organic Fertilizers	Organic acids, salicylic acid, phenolic compounds and water-soluble liquid chitosan	Pannaraj Intertrade, Thailand

biotechnology, and designing opens up the prospects of expanding biomass profitability better use of available natural resources. In the current century, the brilliant horticulture is an approach to fulfilling the need for short- and long-term advancement in the face of environmental change and as a connection to other people (Tomei et al. 1992). It looks to help nations and other practical perspectives in achieving vital agrarian capacities. In the previous few years, explorers identified with the development of assets to a nanometric degree and their native features are sensitive subject in agricultural sector. Basically, when the crystallite size of inorganic materials is decreased to nanoscale, two distinct miracles can happen. In the first (quantum size impact), extreme changes in the physical–synthetic properties of materials are noticed (Tong et al. 2020). For this situation, the presentation is absolutely subject to the semiconductor NPs. Then again, because of the tremendous proportion of surface region to volume, NPs display excellent transduction properties, which are as a rule more intriguing for meaningful reasons for agrarian items. Nanostructure materials uncovered a few benefits in consistent sciences when utilized as transducers or as part of the appreciation on a large-scale estimated detecting gadget. In this reality, the gold NPs (AuNPs) have inbuilt properties, and may be used as transducers for a few enhancements of horticultural items. The AuNPs have a notable surface plasmon band that apparently measures around 520 nm (Sauer 2003). In addition, AuNPs have high surface regions and particular physicochemical resources that can be handily tuned, accordingly making them ideal contenders for creating biosensing gadgets. Also, these NPs have stood out in organic examinations because of their low toxicity, biocompatibility, and novel optical properties. Natural tests estimating the presence or movement have become faster, more tactile and adaptable when the nanoscale particles are assembled. Hence, use of nanoscale particles results in various benefits compared with customary systems (Hawthorne et al. 2014).

3.2 Nanopesticides

The utilization of NMs in plant insurance and creation of food is under-investigated. It is notable that insect vermin are by far the most common in the rural fields; consequently, NPs may play a key role in the control of insects and host microorganisms (You et al. 2017). A new nanoencapsulated pesticide has moderate delivery properties with improved dissolvability, particularity, porousness, and strength. These resources are primarily obtained by either shielding the exemplified dynamic fixings from untimely debasement or expanding their insect control viability for a longer period. Detailing of nanoencapsulated pesticides prompted a decrease in the measurements of pesticides and individuals' openness to them, which is harmless to the ecosystem for crop security (Priester et al. 2012). In this way, improvement of nonharmful and promising pesticide conveyance frameworks for expanding worldwide food production can be achieved while decreasing the negative natural effects on the environment. Microencapsulation-like nanoencapsulation is utilized to build up the nature of the results of the conveyance of wanted synthetic substances to the objective organic cycle. As of late, hardly any compound organizations have transparently advanced nanoscale pesticides available to be purchased as “microencapsulated pesticides.” Some items from Syngenta (Switzerland) such as Karate ZEON, Subdue MAXX, Ospray’s Chyella, Penncap-M, and microencapsulated pesticides from BASF may be fit for nanoscale (Shapiro 2015; Keswani 2020). Syngenta also advertises a few items in Australia, for example, the Primo MAXX, Banner MAXX, Subdue MAXX, etc. Despite being known as miniature emulsions, they are truly nanoscale emulsions. It affirms the delicate interface between the terms microemulsion and nanoemulsion. This procedure is normally utilized for definitions of natural NPs containing dynamic agrochemicals or substances of interest.

3.3 Polymer Composite Materials

Polymers are fundamentally utilized for the controlled arrival of agrochemicals such as insect sprays, pesticides, fungicides, antiseptics, and development energizers. There are different factors such as expense, environment conditions, controlled delivery, straightforward planning, biocompatibility, and biodegradability engaged with modification in polymers for a focused framework or applications (Lade and Shanware 2020). Additionally, steadiness, versatility, glass transition state the nature of polymers, the liquefying point, their similarity to naturally dynamic particles, and the shape and size of the item remain a concern. Then again, these polymers have the likely capacity to control the delivery rate and pace of biodegradability, subsequently being powerful in different end applications, basically medication and agribusiness. The control discharge conduct of the polymeric definition is perhaps the main benefits in the conveyance framework such as medication, agrochemicals, and micronutrients (Al-Dhabi and Valan Arasu 2018). Normally, the controlled delivery framework is principally isolated into two categories: the embodiment of dynamic atoms/agrochemicals/micronutrients by utilizing a polymeric grid and a polymeric lattice, including dynamic particles/agrochemicals/micronutrients, and arrangement of macromolecular spines. A few polymers (common, manufactured, and engineered elastomers, for example, carboxymethyl cellulose, cellulose acetic acid derivation phthalate, gelatin, chitosan, gum Arabic, PLA, polybutadiene, PLGA, polyhydroxyalkanoates, PVA, polyacrylamide, and polystyrene, and so on, are widely utilized in different conveyance frameworks (Peralta-videa et al. 2016; Cobos et al. 2019). Among every one of them, regular polymers are widely utilized for controlled arrival of medications/agrochemicals in light of their ease and being biodegradable. Additionally, controlled delivery rate may be tuned by utilizing diverse sub-atomic weight-based polymers and cross-connecting of various polymers; thus, polymeric composites are proficiently utilized in different natural applications. As of late, NMs have been utilized as nanofertilizers, nanopesticides, and for hereditary progression, treatment of plant infection, and improved development of the plants (Sánchez-López et al. 2020). All in all, polymers embodied with different materials including metal NPs, carbon-based NMs, organic particles, agrochemicals, pesticides, insect poisons, etc., with controlled delivery practices improve the biocompatibility of the materials, are simple for use and subsequently successfully utilized in different end applications, primarily medication and horticulture (Faisal et al. 2018).

3.4 Nanofungicides

Parasitic diseases among crops have a detrimental effect on the creation. Despite the fact that various fungicides are available on the market, their application has a negative impact on plants. Nanotechnology can assume a vital part in taking care of this issue. NPs have been testing as antifungal specialists against pathogenic organisms. Antifungal action of NPs of zinc oxide (35–45 nm), silver (20–80 nm), and titanium dioxide (85–100 nm) has been tried against *Macrophomina phaseolina*, a significant soil-borne microorganism of heartbeat and oilseed crops (Tan et al. 2018; Rastogi et al. 2017). The higher antifungal impact was seen in silver NPs at lower fixations than zinc oxide and titanium dioxide NPs. Maize treated with nanosilica (20–40 nm) has been evaluated for opposition against phytopathogens, *Fusarium oxysporum* and *Aspergillus niger* as contrasted native silica properties. Nanosilica-treated plants showed a higher articulation of phenolic compounds in gathered leaf extracts and a low articulation of stress-responsive catalysts against these organisms (Landa et al. 2017). These outcomes showed essentially higher opposition in maize treated with nanosilica compare to the other products constituting disorders related to phenols, phenylalanine alkali lyase, peroxidase, and polyphenol oxidase, at 10 and 15 kg/ha. Therefore, silica NPs can be utilized as an option powerful antifungal specialist against phytopathogens. The silver has much higher antifungal movement than different metals. This is based on the fact that silver particles cause the inactivation of cell divider thiol gatherings of parasitic cell dividers bringing about disturbance of transmembrane, energy digestion, and electron transport chain. Transformations in contagious DNA, separation of the protein edifices that are fundamental for the respiratory chain, decreased layer porousness, and cell lysis are likewise different instruments (Hernández-Hernández et al. 2018). The adequacy of silver NPs is subject to molecule size and shape and diminishes with expanding molecule size. It has been tracked down that a shortened three-sided molecule shape showed more noteworthy “cidal” impact than round and pole-formed particles. Aditionally these fungicides are utilized as the potent pest controller in the agricultural sector for better productivity and disease free products because of a good bond on the bacterial and contagious cell surface (Vinkovic et al. 2017).

3.5 Nanoherbicides

Weeds are the greatest danger in agribusiness and decrease the yield of harvest by a noteworthy amount as they utilize the supplements that are accessible to the crops. Destroying weeds by traditional methods is tedious. There are various herbicides accessible financially. They kill the weeds in the fields, but they also harm the crop plants. They are additionally capable of diminishing the fruitfulness of the soil and contaminating it (Van Nhan et al. 2015). Nanoherbicides can assume a vital role in eliminating weeds from crops in an eco-accommodating way, without leaving any unsafe build-ups in soil and climate. Some of the common nanoherbicides are elaborated in Table 2. Embodiment of herbicide in polymeric NPs likewise brings about ecological wellbeing. Unbalanced utilization of herbicides for longer periods of time leaves deposits in the soil, which cause harm to successive harvests. Ceaseless utilization of the same herbicide for a consistent timeframe causes weeds to build up obstruction against the herbicide. The adequacy of nano zerovalent iron has been evaluated to dechlorinate herbicide atrazine (2-chloro-4ethylamino-6-isopropylamino-1,3,5-triazine) from atrazine-debased water and soil (Ali et al. 2018). Target-explicit NPs packed with herbicide have been produced for conveyance into the underlying foundations of weeds. These atoms go into the roots system of the weeds, move to the cells, and restrain metabolic pathways such as glycolysis (Marslin et al. 2017). This eventually prompts the plants to die. The toxicity of poly (ε-caprolactone) nanocapsules containing ametryn and atrazine against the alga *Pseudokirchneriella subcapitata* and the microcrustacean *Daphnia similis* has been tried. Herbicides exemplified in the poly(ε-caprolactone)

Table 2 List of commercial polymeric composite nanopesticides/nanoherbicides and their application

S. No.	Polymer carrier system	Method of synthesis	Active ingredients	Application
1	Chitosan	Entrapment/ encapsulation	Imazapic and imazapyr	Cytotoxicity evaluation
2	Silica	Suspension	Imidacloprid	Assay of perfused brain tissue and cells
3	Alginate	Emulsion	Imidacloprid	Cytotoxicity assay
4	Wheat gluten	Entrapment/ extrusion	Ethofumesate	Diffusivity reduction
5	Carboxy methyl chitosan	Encapsulation	Methomyl	Evaluate control release pattern
6	Surfactants/ oil/water	Emulsion	Glyphosate	Increase in bio efficiency and reduction of the environmental toxicity of pesticides
7	Organic/inorganic nano hybrid carriers	Self-assembly	2,4-dichlorophenoxyacetate	Control release pattern observation

nanocapsules brought about lower harmfulness to the alga (*Pseudokirchneriella subcapitata*) and higher toxicity to the microcrustacean (*Daphnia similis*) in contrast to the herbicides alone (Chung et al. 2019).

3.6 Nanobiosensors

Numerous benefits of physical–compound properties of nanoscale materials are additionally exploitable in the field of biosensors advancement. It was assessed that the affectability and execution of biosensors can be improved by utilizing NMs through new potential innovation. The enormous headway that has been made in nanobiosensors is because of the incredible innovative interest in quick, delicate, and practical nanobiosensor frameworks in crucial spaces of human movement, for example, medical services, farming, genome examination, food and drink, interaction ventures, natural checking, protection, and security (Mazaheri Tirani et al. 2019). As of now, the nanotechnology-based biosensors are in the beginning phase of improvement. The improvement of instruments and methods used to create, measure, and picture nanoscale objects has prompted the advancement of sensors. NMs such as metal (gold, silver, cobalt, etc.) NPs, CNT, attractive NPs, and QDs have been effectively explored for their applications in biosensors, which have become another connecting link between natural identification and material science. Accordingly, a biosensor is a gadget that joins a natural acknowledgment component with physical or synthetic standards. It incorporates an organic part with an electronic part to yield a quantifiable potential product, and the natural acknowledgment is through the transducer cycle through electronic accomplishment (JuárezMaldonado et al. 2018). The higher explicitness and affectability of biosensor frameworks over the customary strategies are because of the presence of the bioreceptor (natural component) that is joined with a reasonable transducer, which delivers a sign after communication with the objective premium particle. As of late, extraordinary regular and counterfeit bioreceptors have been created and applied, such as chemicals, dendrimers, thin films, etc. Hence, a biosensor, a logical gadget, converts a natural reaction into an electrical sign (Raigond et al. 2017). The transducer and the related hardware or sign processors are essentially answerable to the location of the capacities. The miniature cantilever-based DNA biosensor that utilizes AuNPs has been created and utilized generally to identify low-level DNA fixation during a hybridization response.

3.7 Quantum Dots

Quantum dots are obviously better and quicker than natural fluorescent colors because of a more proficient glow, few emanation spectra, brilliant photostability, and validity as per the molecule sizes and material pieces. By a solitary excitation light source, QDs can be responsive to all tones because of their wide retention spectra. Quantum dots have been utilized to recognize microorganisms related to various plant diseases (du Jardin 2015). Quantum dots fluorescent reverberation energy motion-based sensors have been created to distinguish witch's broom disease of lime brought about by *Phytoplasma aurantifolia*. The immunosensor created showed a high affectability, particularity of 100%, and a location cutoff of ca. 5 *P. aurantifolia* per μL. Rhizomania is the most dangerous infection in sugar beet brought about by beet necrotic yellow vein infection. *Polymyxa betae* (Keskin), the only known vector of beet necrotic yellow vein infection, for transmission of the infection to the plants was effectively identified by quantum specks fluorescent reverberation energy motion-based sensors (Vazquez-Hernandez et al. 2019). To distinguish organophosphorus pesticides in vegetables and natural products; the optical transducer of cadmium telluride semiconductor quantum dabs coordinated with acetylcholinesterase protein by the layer-by-layer gathering strategy. This brought about a profoundly delicate biosensor dependent on a chemical hindrance instrument, which was far superior to the regular gas chromatography techniques or amperometric biosensors. Interesting optical property of thiol-balanced out radiant cadmium telluride (CdTe) quantum dabs has been utilized to identify methyl parathion at picogram levels (Worrall et al. 2018). Water-solvent CdTe QDs and profoundly silica nanosphere encapsulating cadmium telluride quantum dots have been utilized as a biosensor for assurance of deltamethrin in leafy foods tests.

3.8 Nanobarcodes

Nanobarcode particles are made through a semi-mechanized and profoundly adaptable cycle of electroplating of inactive metals such as gold and silver, into layouts characterizing molecule measurement and in this manner nanorods are delivered. These nanobarcodes are utilized as distinguishing proof labels for multiplexed investigation of quality articulation (Panattoni et al. 2013). Nanotechnology has helped to make headway in the field of biotechnology and has resulted in improvement in plant protection from ecological burdens such as dry spells, saltiness, and diseases. Nanotechnology-based quality sequencing is equipped for quick and practical identification and use of characteristic assets of plant quality (Hoseinzadeh et al. 2016).

3.9 Micronutrient Supply

Micronutrients such as manganese, copper, boron, iron, molybdenum, and zinc are significant for development and advancement. A significant increment of harvest yields and new cultivation practices has dynamically diminished the micronutrients of soil such as zinc, iron, and molybdenum. Foliar use of micronutrients can improve take-up by the leaves. Nanotechnology can be utilized to make micronutrients accessible to plants (Siddiqi and Husen 2017). Nano details of micronutrients can be accomodated on plants or can be provided in the soil for take-up by roots to upgrade the soil quality and strength. The arrival of 1-naphthylacetic acid (a significant plant development chemical) from chitosan NPs has been tried at various pH values and temperatures. The definition was found to have potential for the late delivery arrival of agrochemicals. Distinctive NPs have been tried to provide a suitable level of micronutrients in plants (Wang et al. 2013). Iron deficiency is an inescapable issue in plants in predominantly high pH and calcareous soils. Foliar utilization of iron mixtures with the innovation of NPs might be an answer to the issue. The impact of utilization of iron oxide nanoparticles on the reaction of wheat development, yield, and quality has been evaluated. The delivery of iron oxide arrangement have been utilized at five levels (0, 0.01%, 0.02%, 0.03%, and 0.04%) to check the impact on spike weight, 1000 grain weight, biologic yield, grain yield, and grain protein content. Expansion in these attributes was found when compared with controls (Molnár et al. 2018). Expansion in chlorophyll substance in sub-apical leaves of soybeans in a nursery test under aqua-farming conditions has been attributed to utilizing low groupings of superparamagnetic iron oxide NPs. This test presumed that iron oxide NPs could be utilized as a wellspring of iron for soybeans to reduce chlorotic indications of iron insufficiency. Foliar use of 500 mg L^{-1} iron NPs to peas observed in the dark essentially increased the quantity of pods per plant (by 47%), weight of 1000 seeds (by 7%), the iron substance in leaves (by 34%), and chlorophyll content (by 10%) over those of the controls. Utilization of iron NPs also improved yield more than use of a customary iron salt (Kharissova et al. 2019). These boundaries were expanded by 28%, 4%, 45%, and 12%, individually, under the iron NPs treatment compared with those under treatment with iron salt. Likewise, iron NPs fundamentally improved the advantageous impact of magnesium NPs utilized as nanofertilizer in peas observed in the dark. For an ideal development, the vast majority of the plants commonly required 1–5 mg L^{-1} iron in soil arrangement. Upgraded development of mung bean (*Vigna radiata*) and photosynthesis have been attributed to manganese NPs. Improved development of mung bean and chickpea *(Cicer arietinum)* seedlings at a low focus utilizing zinc-oxide NPs with plant agar strategy was noticed; a decrease in the development paces of roots and shoots was observed in the yields and crop plants (Singh et al. 2018).

3.10 Insect Pest Management

Engineered agrochemicals have changed the substance of horticulture; a new test insect pest management has also been developed. NPs have an incredible guarantee for the administration and control of insect pests in current farming. Insecticidal action of garlic fundamental oil against *Tribolium castaneum* (red flour beetle) has been expanded by polyethylene glycol-covered NPs. Utilization of this detailing of the control adequacy against adult *T. castaneum* was determined to be about 80%, which was apparently because supported arrival of the dynamic parts of the NPs (Krumpfer et al. 2013). Uses of various types of NPs, for example, silver NPs, aluminum oxide, zinc oxide, and titanium dioxide, in the control of rice weevil (brought about by *Sitophilus oryzae*) and Grasserie disease in silkworm (brought about by *Bombyx mori* and baculovirus BmNPV (*B. mori* atomic polyhedrosis infection) were examined. They further contemplated the change in *Bombyx mori* nucleopolyhedrovirus by lipophilically covered silica NPs, aluminum NPs in the hexagonal close-packed α structure and aspartate-covered gold NPs in *B. mori* cell lines utilizing cytopathic impact and plaque decrease measures (Baun et al. 2017). A moderate polyhedra roughening was noticed for aluminum NPs, but no roughening was seen for gold NPs. At the point when mulberry leaves *(B. mori*) were treated with ethanolic suspension of hydrophobic alumino-silicate NPs, a huge decline in viral burden occurred. Insecticidal action of nanostructured aluminum against *Sitophilus oryzae L.* furthermore, *Rhyzopertha dominica* announced critical mortality following 3 days of persistent openness to nanostructured aluminum-treated wheat. Thus, financially accessible insect toxins, inorganic nanostructured aluminum, may provide a modest and solid option for the control of insect pests. The entomotoxicity of silica NPs was tried against rice weevil *Sitophilus oryzae* and the adequacy and mass measured silica (single particles bigger than 1.0 μm) were compared (Mody et al. 2010). Shapeless silica NPs were discovered to be exceptionally compelling against this insect, causing over 90% mortality, demonstrating the adequacy of silica NPs to control insect pests. The nano-epitome of pesticide permits appropriate assimilation of the substance into the plants because of moderate and supported delivery and has a dependable and determined impact, not at all like the typical agrochemicals. Manufactured pesticides have impeding ecological effects, yet their specificity toward the focus on irritations is high. Thus, there is a need for a move toward herbal insect sprays utilizing nanotechnology for better pest control.

4 Polymeric Complexes

Polymers are predominantly utilized for the controlled arrival of agrochemicals such as insect poisons, pesticides, fungicides, antiseptics, and development energizers. There are different factors such as expense, environment conditions, controlled delivery, basic equation, biocompatibility, and biodegradability engaged with modification in polymers for focused framework or applications. Additionally, high strength, unique structure and glass transition state, nature of polymers, softening point, its similarity to naturally dynamic atoms, and the desired shape and size of the item remain concerns. Then again, these polymers have the expected capacity to control the delivery rate and pace of biodegradability, thus being powerful in different end applications, primarily medication and farming (Vinkovic et al. 2017). The control discharge conduct of the polymeric definition is quite possibly the main benefit in the conveyance framework such as medication, agrochemicals, and micronutrients. All in all, polymers typified by different materials including metal NPs, carbon-based nanomaterials, organic particles, agrochemicals, pesticides, insect sprays, with controlled delivery practices, improve the biocompatibility of the materials and are potent for dvelopemnt of agricultural scetor and subsequently adequately utilized in different end applications, primarily medication and horticulture. The various polymeric composites employed in the agro-biomedical fields are described in the following subsections.

4.1 Polymer Metal Complex

The metal NMs such as Cu, Zn, Fe, titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), aluminum nitride (AlN), boron nitride (BN), and zinc oxide (ZnO), are widely utilized for plant development and security of harvests. Generally, NMs are incorporated in order to provide the controlled delivery conveyance framework for agrochemicals that improved solvency and secured organically dynamic atoms against early corruption, along these lines improving the adequacy of agrochemicals even at lower dosages. In any case, these metal NMs amass with respect to the root and move inside the shoot and leaf less (Fig. 2) (Zhang et al. 2018). In addition, agglomeration, flimsiness, and trouble utilizing in a straightforward way on land remain concerns. In this unique situation, the consistent dvelopment of new breeds of agricultural products give rise to the expanding horizon of potent product for the sustained devlopemnt of agricultural sector to different end applications such as clinical, climate, sensors, and agribusiness.

There are various existing materials such as plastics, metals, earthenware, and polymers, that cannot accomplish mechanical necessities for various applications.

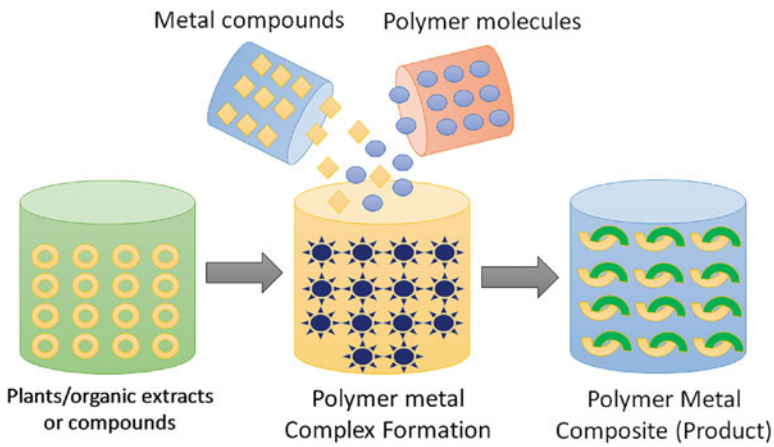

Fig. 2 Schematic representation of polymer metal composite formation

Typically, hybrid NMs containing different NMs as a filler with the polymeric lattice hold extraordinary interest in light of different benefits such as high biocompatibility, controlled delivery, dependability, and nontoxicity (Abdal Dayem et al. 2017b). The main ruling methodology for the union of a metal–polymer composite by utilizing metal/metal oxide typified by polymers creates the ideal item. The improvements of hybrid or devloped plants species by utilizing filler-polymer associations at the interface just as the uniform scattering of the NMs inside the polymeric network. Generally, there are three ways to deal with and accomplish these necessities: adjustment of fillers/NM properties, modification of polymer properties by functionalization or arrangement of co-polymers, and creating desired properties with hybrid materials/polymeric nanocomposites. Based on horticultural applications, polymeric covering or polymeric nanocomposite is significant, as higher convergence of NMs may cause some degree of damage inside the plants (Wang et al. 2017).

4.2 Polymer Carbon Complex

Carbon-based NMs displayed different end applications such as natural remediation, sensors, drug conveyance, antibacterial specialists, crop assurance, and development control of the plants because of novel qualities, mostly optical, electrical, mechanical, and heat properties. Huge improvement has been made in the amalgamation of carbon-based NMs such as actuated carbon, initiated carbon filaments, CNTs, CNFs, graphene, and fullerenes, which hold incredible interest in farming because of their opportunity as a development energizer and to secure harvests (Moreno-Altamirano et al. 2019). Besides, these carbon-based NMs, basically CNTs, and CNFs, have the possible capacity to enter the seed coating and move inside the plants from root to shoot to leaves. A few reports proposed that CNTs and CNFs proficiently move inside the plants. These examinations suggested that carbon-based NMs acted as a development energizer by expanding the take-up of water and supplements. Strangely, CNFs hold metal NPs and the arrival of metal NPs in a controlled way (Mazzon and Marsh 2019). These metal NPs such as Cu, Zn, and Fe also acted as micronutrients for the plants; in this manner, CNFs acted as transporters for micronutrient conveyance. Additionally, CNFs increase the water take-up capacity, germination rate, and nontoxicity even at higher centralization of the portion and consequently are utilized as development energizers of the plants. In a new report, the CNFs are utilized as a transporter to convey acylated-homoserine lactone in chick pea plants. The investigation recommended that CNF-acylated homoserine lactone-based composite expanded the plant development as well as the stress resilience capacity (Lysenko et al. 2018). The CNFs may be new-age manures that improve development of the plants and protect from external damage, too. Notwithstanding, direct utilization of the carbon-based NMs still remaining partly a worry. To defeat such issues, carbon-based NMs are epitomized by polymeric composites for the rural conveyance framework. Bi-metallic (Cu/Zn) NP-scattered CNFs embodied with PVA-starch composite were combined to deliver polymer-bi-metal-carbon (PBMC) composite. The delivered PBMC polymeric composite is viably used as a compost that improves the development of the plants. The investigation also recommended that the arrival of micronutrients from PBMC is moderately delayed in examination with CNFs because of the embodiment of polymers. Also, CNFs proficiently moved through the roots to the shoots to the leaves of the plants. The delivered biodegradable PBMC-based detailing conveying Cu/Zn-CNFs (micronutrients) opens up more current methodology on the use of NMs in horticulture (Galdiero et al. 2011; Mori et al. 2013).

4.3 Polymeric Nanorods

Multifunctional plasmonic materials that can couple to diagnose for the deviation and size dependent transport and, can be combined with micro-electromechanical systems, and incite explicit field reactions. The gold nanorods (Fig. 3) completely physiological changes occurred in watermelon plants and affirmed phytotoxicity toward the plant, especially at a high focus, and furthermore the capacity to move auxin development controller 2,4-D, which had a critical effect on the guideline of tobacco cell culture development (Rezatofighi et al. 2015).

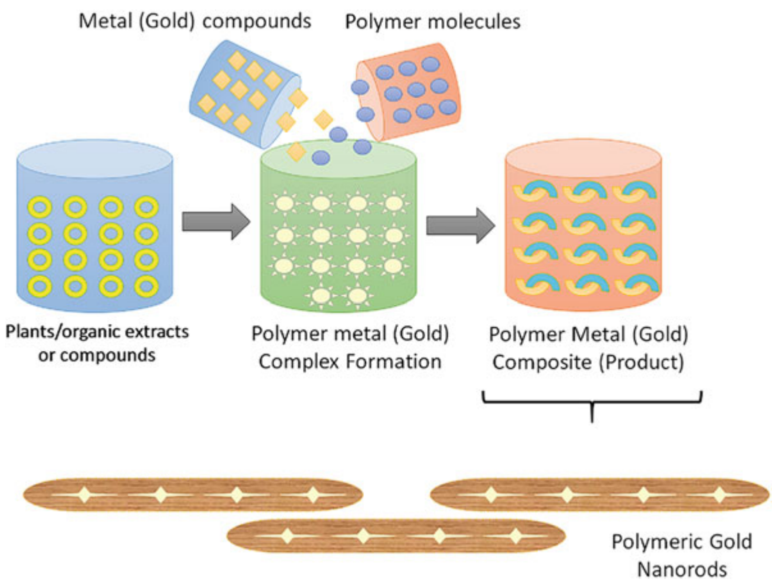

Fig. 3 Schematic representation of the polymeric metal (gold) nanorods formation method

4.4 Miniature and Nanoencapsulation

Embodiment is characterized as an interaction in which the given item is encircled by a covering or inserted into a homogeneous or heterogeneous framework; consequently, this cycle results in cases with numerous valuable properties. The advantages of embodiment strategies are for assurance of substances/objects from unfriendly conditions, for controlled delivery, and for precise focus. Contingent upon the size and state of containers, distinctive embodiment advances are referenced, whereas the (full-scale) epitome/covering results in cases in macroscale, although miniature and nanoencapsulation will result in particles in micro- and nanoscale size (Khandelwal et al. 2014). Nanocapsules are vesicular frameworks in which the substances are bound to a depression comprising an inward fluid center encased by a polymeric film. As of late, miniature and NPs stand out enough to be noticed for the conveyance of medications, for assurance and expansion in the bioavailability of food sectors or nutraceuticals, in food sectros and in material fields, and furthermore it has more advantages in plant science. A few medications, for example, peptides or calming compounds are effectively nanoencapsulated. The improvement of nanoencapsulated techniques for the ligation of focused tissues to NPs will make it possible to convey a few organically dynamic mixtures to the objective tissues (Baram-Pinto et al. 2009). Moreover, the improvement of this innovation will build greater opportunities to make new medications with exact helpful activity on affected tissues. Nanocapsules can conceivably be utilized as MRI-guided nanorobots or nanobots.

4.5 Polymeric Nanoemulsions

Nanoemulsions are shaped by little emulsion nanoscale beads (oil/water framework) showing sizes less than ~100 nm (Fig. 4). Although in a general sense critical contrasts among nanoemulsions and microemulsions could not exist, the actual properties of nanoemulsions can be not quite the same as those of microscale emulsions. Because of the size of the drops, the proportion of the surface region to volume, the, shear stress, and flexible modulus of nanoemulsions are fundamentally bigger than those of customary emulsions (Broglie et al. 2015). In addition, dissimilar to general emulsions, the majority of nanoemulsions occur in an optically straightforward manner, and in fact have numerous benefits make these more functional. Surprisingly, the detailing of nanoemulsion needs high energy; subsequently, it requires some uncommon gadgets that can create excessive shear pressure, for example, a high-pressure homogenizer or ultrasonic generator, announced as a "low-energy" technique for the arrangement of nanoemulsions. In this cycle, two fluid stages (one is a homogeneous fluid comprising lipophilic stage and hydrophilic surfactant in addition to possibly a dissolvable, polymer or drug, and the other is a watery stage, or even unadulterated water) are coinjoin for more

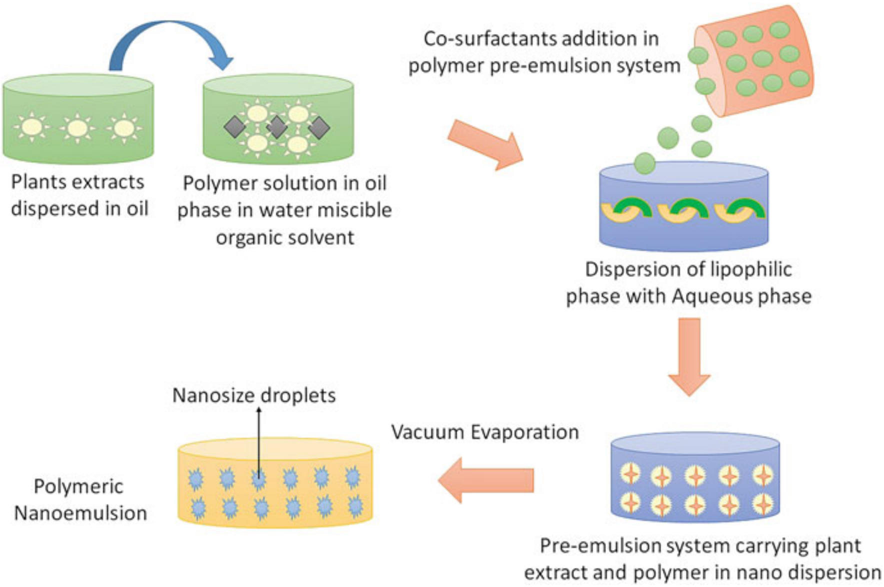

Fig. 4 Schematic representation of polymeric nanoemulsion synthesis mechanism for agricultural application

funstional synthesis (Zhong et al. 2019; Levina et al. 2016). At that point the hydrophilic species contained in the slick stage is quickly solubilized into the watery one, instigating the demixation of the oil as nano-beads, immediately balanced out by the amphiphiles. This technique subsequently appears to be least difficult and does not need any exceptional high-energy gadgets.

5 Communication of Polymeric Nanocomposites with Plants

Communication of polymeric nanocomposites with plants (aggregation, take-up, and movement), relies upon different factors such as shape, size, surface charge, dependability, synthetic nature, useful gathering, and the types of the plants. The cell mass of the plants is one of the significant destinations of association with NMs/different micronutrients. The cell-divider does not allow any unfamiliar particles including NMs/different micronutrients, as it moves about as an actual obstruction (Cui et al. 2010). The plant cell divider contains phosphate, hydroxyl, carboxylate, sulfhydryl, and imidazole clusters that produce complex biomolecules, and specific movement and take-up along these lines. There are two principal properties that influence the take-up and movement of NMs/different micronutrients, i.e., surface charge and size. The surface charge of the NMs/different micronutrients is one of the significant boundaries. The adversely charged NMs/different micronutrients may support movement and take-up inside the plants because of contrarily charged plant cell-dividers (Tripathi et al. 2017). The contrarily charged NMs/different micronutrients and plants do not draw in one another; in this way there is effective take-up and movement of the materials. Then again, emphatically charged NMs/different micronutrients and adversely charged plant cell-dividers draw in one another, subsequently aggregating on the root surface. The metal NPs are emphatically charged, in this manner having high amassing and less movement capacity. In addition, these metal NPs show phytotoxicity at a higher focus because of aggregation. The size of the NMs/different micronutrients is one of the significant variables for take-up and movement (Avellan et al. 2019). The more modest size (20–200 nm) favors the take-up and movement inside the plants. Besides, carbon-based NMs such as CNTs and CNFs measuring ~500 nm or less effectively move inside the plants because of their development across the epidermis through the cortex to the vascular group. The NMs are moved to attach through the shoot to the leaves through cell-divider organization and plasmodesmata. The thin movements and osmotic powers are likewise one of the main thrusts of movement of NMs inside the plants (Ali et al. 2016). Furthermore, the kinds of NMs and compound synthesis additionally influence the take-up and movement inside the plants. The functionalization and covering of NMs change the adsorption and collection capacity inside the plants. A portion of the NMs may collect at the Casparian strip, through another move with symplastic pathways toward the shoot and root. As of late, carbon-based NMs such as CNTs and CNFs were transporters for qualities/micronutrients/biomolecules inside the cells. Different examinations are performed to comprehend the specific component behind the NM take-up and movement (Truong et al. 2015). The larger estimated NMs cannot enter the cell dividers; notwithstanding, an examination of *Arabidopsis thaliana* leaf recommended the formation of endocytosis-like structures in plasma film. Liu et al. proposed that water-soluble SW-CNTs of ~500 nm (length) were uncovered on *Nicotiana tabacum*. The water-soluble SW-CNTs can infiltrate through unbending and fundamental cell dividers. By and large, a few components, including surface charge, size, compound nature, and surface covering impact the take-up and movement capacity inside the plants. Additionally, functionalization of NMs with synthetics/polymers may change the properties of materials, in this way effectively moving inside the plants (Raliya et al. 2016).

6 Polymeric Nanomaterial Improved Hereditary Designing

Hereditary designing of the plant framework is fundamentally an endeavor of ecological supportability, amalgamation of the item, and the designing of rural yields; in this manner, progression of hereditary designing is fundamental for a developing populace. The quality alteration incorporates different methods to use to precisely change the genome grouping. The rise of quality alteration is an energizing methodology particularly for farming researchers in light of the basic cycle and preciseness that can create an improved assortment of harvests (expansion of important attributes and erasure of opposing characteristics) (Dasgupta et al. 2014). With the assistance of genome altering/hereditary designing, specialists continue to focus on the improvement in the yield of the harvests with unfriendly conditions such as changes in the environment. Generally, the cell mass of the plants is addressed as an actual hindrance; along these lines, conveyance of biomolecules/qualities is quite tedious and challenging (Agarwal et al. 2015). Generally, two methods of changing qualities exist in the plant framework, i.e., payload conveyance that relies upon the conveyance strategies and recovery by utilizing changed plants, which relies upon the tissues, advancement of the conventions, and confounded chemical blends. Nonetheless, the current innovations have a great deal of impediments such as less change, great harmfulness, and DNA coordination into the genome. The stupendous difficulties of qualities/biomolecules load conveyance inside the plant framework because of the presence of inflexible and diverse plant-cell dividers mean that there is a consequently slower change of qualities/biomolecules inside the plants (Chhabra and Kumar 2019). To conquer such issues, two methodologies have been created and utilized for change of qualities/biomolecules inside the plants, i.e., an agrobacterium-mediated conveyance framework and biolistic molecule transformation (DNA bombardment). Notwithstanding, these methodologies additionally have different downsides/impediments such as species reliance (changing the species changed the proficiency), required recovery from tissues, in this manner tedious and less effective, and agrobacterium-interceded qualities/biomolecule change may present unfamiliar hereditary materials. The agrobacterium-interceded qualities/biomolecules may cause disturbance of qualities/poor/flimsy quality articulation because of the arbitrary DNA incorporation (Bhatt and Kumar 2017). The DNA mix may be forestalled by utilizing non-integrated infections or plamid less transport DNA. In this manner, these two techniques are more favored instruments in an examination of other ordinary strategies. In this specific situation, nanotechnology may be an elective device to determine such issues related to the current conveyance framework. Different NM-constructed plant conveyance frameworks with respect to the blend of NMs, agrochemical conveyance framework, micronutrient conveyance framework, and movement of NMs increased the development of plants by utilizing metal-based NPs, CNTs, CNFs, QDs, graphene and its subsidiaries, and fullerenes. Then again, some NMs displayed phytotoxicity because of the oxidative pressure and vascular blockage, harming the underlying DNA. As of late, created NM-interceded biomolecule conveyance framework for quality articulation (Buzea and Pacheco 2017). For this, DNA was united on covalently functionalized immaculate SW-CNTs and MW-CNTs to create successful DNA conveyance with solid articulation of protein in developing *Eruca sativa* (arugula) leaves. The DNA is conveyed in the plant core with the CNTs and furthermore de-exploring of practical quality, independently. The uniting of DNA is done on CNTs owing to the π-π stacking; the SDS is supplanted by adsorption DNA by utilizing the dialysis cycle. The created DNA–CNT-based conveyance framework is tantamount to an agrobacterium-interceded conveyance framework. The investigation additionally recommended that the created CNT-based conveyance framework proficiently communicates protein in arugula protoplasts (cell-divider free) with a change (85%) in effectiveness. For this, the reserch fraternity shaped the complex of DNA NPs and conveyed them into the dust grains by utilizing magnetic force (Bhushan 2017). These investigations recommended that NM-based conveyance framework assumes a huge part in the progression of the hereditary designing of the plant framework. As a rule, hereditary designing of the plant framework is a more potent in practical platform. The methodology of the qualities/biomolecule change inside the plants actually remains a concern owing to the multi-faceted and inflexible cell divider. There is an absence of the powerful conveyance of the different qualities/biomolecules inside the plant framework without harming the tissues. Nanotechnology may be an elective instrument in the progression of hereditary designing in plant frameworks that settle such a conveyance challenge of qualities/biomolecules, accordingly expanding the utility of hereditary designing (Fig. 5) (Zhang et al. 2015; Ebbs et al. 2016).

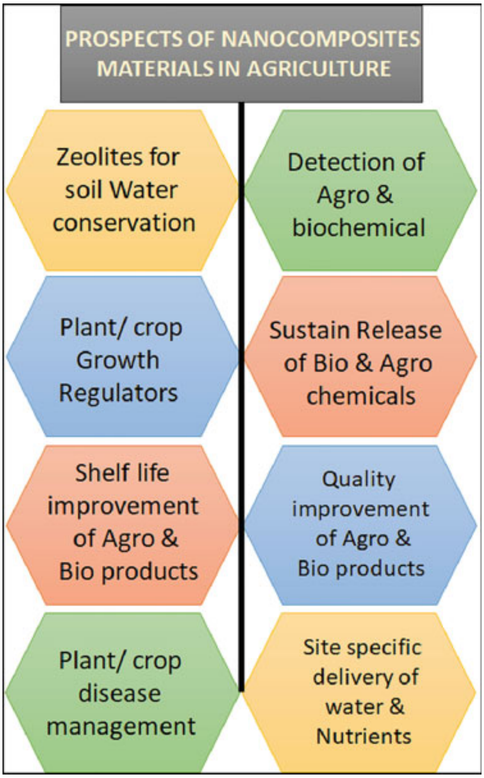

Fig. 5 Illustration of prospects of nanocomposite materials in agricultural applications

7 Conclusion and Future Prospects

Horticulture, which is the lone supplier of human food, should be created from momentary and lasting contributions with notable advances. Subsequently, it is important to obtain cutting edge information in agribusiness. Despite being relative advantages in agribusiness measure, really non-modern countries are encountering a shortfall of high meaning of food things. Polymeric nanocomposites have the unmistakable advantages of biodegradability and biocompatibility, which make them ideal materials to be utilized in crop assurance and micronutrient conveyance in the field of horticulture field (Bradfield et al. 2017). The receptive NMs have been utilized in different applications as a result of their utilitarian gatherings and qualities; accordingly, engineered nanomaterials may have the likely capacity of being utilized in various applications, including horticulture. Also, the exemplification of polymers with various NMs such as metal/metal-oxide- and carbon-based NMs improved the controlled delivery practices, biocompatibility, and basic use (Yarizade and Hosseini 2015). In this way, they are proficiently utilized in different applications, predominantly in agribusiness. Moreover, take-up, collection, and movement capacity of the NMs primarily rely upon surface charges, size, and substance nature of the materials. From one perspective, polymeric covering of NMs may change the usefulness and surface charge; hence, polymeric composite may effectively move inside the plants. As for progress in hereditary designing, NMs may be elective devices that effectively convey qualities/biomolecules. In this manner, polymeric nanocomposite improves the utility of hereditary designing in plant framework. As talked about in the content, CNFs are cutting edge compost that can without much of a stretch convey micronutrients and biomolecules inside the plant (Hasanuzzaman et al. 2020). Regardless, difference in these assessment into field, a couple of issues ought to be discussed or organized considers required i.e., cost of nanofertilizers, wellbeing concerns such as ecological damage, and simple applications. We need to carry out more exploration in such farming territories for more approachable techniques in the field (Vannini et al. 2013).

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Part III
Agronanobiotechnology

Nanotechnology: A Tool for the Development of Sustainable Agroindustry

Rabia Javed, Muhammad Bilal, Joham Sarfraz Ali, Sosun Khan, and Mumtaz Cheema

1 Introduction

Nanotechnology is a rapidly emerging field having diverse applications. Nanoparticles possess <100 nm size and distinguishing physical and biochemical characteristics from bulk materials (Salata 2004). The modern techniques of nanotechnology have significant potential to address the issues and shortcomings of conventional agricultural practices. For example, nanofertilizers, nanosensors, nanopesticides, and nano-food packaging are crucial in enhancing yield and quality, plant protection, and shelf life of crops (Javed et al. 2022a). Also, the applications of nanoparticles in nutrient delivery, seed germination and plant production, metabolomics, and genetic transformation have paramount significance (Duhan et al. 2017; Javed et al. 2021). Hence, the utilization of nanotechnology in different areas of agriculture sector can altogether increase its production since it not only increases the growth of the plants but also protects them from different pests or harmful chemicals, ultimately ensuring improved quality of food and curtailing the crop waste (García et al. 2010; Jampílek and KráL'Ová 2015). Besides, the nanoparticle-based agricultural approaches of biotechnology ensure the controlled and sustained release as well as targeted delivery of active ingredients (Duhan et al. 2017).

Nanotechnology has also the potential of remediating toxic soil contaminated with heavy metal pollutants like cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), and arsenic (As) by combining with other techniques like phytoremediation. Such

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metals and metalloids are very difficult to be removed from soil and are dangerous for human health. Hence, nanoremediation plays a crucial role in eliminating these hazardous chemicals (Baranowska-Wójcik et al. 2020). Finding out the toxicity range of novel nanomaterials is essential to be assessed by the detailed studies on nano-bio interactions. In this way, the surrounding living and non-living environment is saved from the unanticipated risks eventually affecting the human life. The chances of public acceptance of new nanoproducts also get increased (Foster et al. 2011; Adeel et al. 2020).

This book chapter encompasses the overview of impact of nanoparticles on the agricultural biotechnology and agroindustry. It also highlights the challenges faced by the plant scientists regarding usage of nanobiotechnological products due to their toxicity and less acceptance by the farmers, technicians, and general public.

2 Nanofertilizers

Nanofertilizers are products of nanotechnology that provide nutrients—micronutrients, such as sulphur (S), calcium (Ca), magnesium (Mg), nitrogen (N), and potassium (K), plus macronutrients, like zinc (Zn), iron (Fe), and manganese (Mn)—to young or growing plants in order to aid them in their growth and to enhance their production (Elemike et al. 2019). Nanoparticulate fertilizers include carbon nanotubes (CNTs), and titanium dioxide (TiO_2) and silicon dioxide (SiO_2) nanoparticles (Chhipa 2017). Nanofertilizers are beneficial over conventional fertilizers as they are non-toxic, environment-friendly, and cost-effective. They enhance the quality parameters of plants along with increasing plant fertility (Qureshi et al. 2018). The high surface-to-volume ratio as well as smaller size increases the possibility of amount of particles per area of fertilizer with greater penetration, and absorption of nutrients and their bioaccessibility to plant parts, hence increasing nutrient use efficiency (Singh et al. 2017). Due to these characteristics, nanofertilizers' application may reduce nutrient leaching losses compared to conventional fertilizers that are more prone to leaching and consequently contaminate fresh water resources and aquifers jeopardizing environmental safety. The nano size of nutrients not only helps the plants to grow more effectively but also aids in accumulation of nutrients that resultantly terminates the problem of nutrient deficiency. Nanofertilizers are somewhat more than an agricultural revolution as they ensure fertility of land by providing nutrients to unfertile lands (Jampílek and KráL'Ová 2015; Khan and Rizvi 2017). Examples of few commercialized nanofertilizers have been shown in Fig. 1.

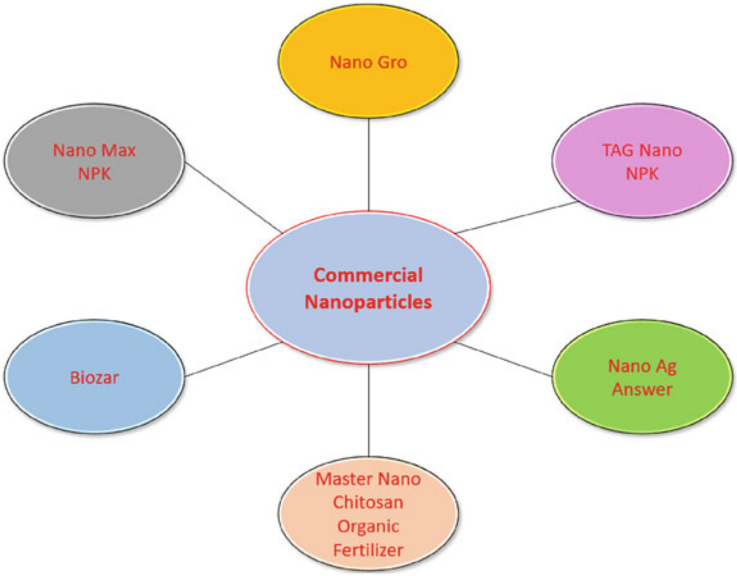

Fig. 1 Examples of few commercial nanofertilizer products

3 Nanopesticides

Pesticides play a significant role in saving biological disasters by improving crop production and maintaining steady growth of crop plants. According to the statistical studies done by the Food and Agriculture Organization (FAO) of the United Nations (UN), total 30% global output has been recovered on all products of agriculture using pesticides that control pathogens and pests. However, there are shortcomings associated with the use of conventional pesticides, which is threating human health and environmental safety (Zhao et al. 2018). Therefore, new product development with new plant protection formulations to withstand problems associated with conventional pesticides is essential. Recently, researchers are working on nanopesticides having superior properties such as no permanent degradability, more solubility, thermal stability, and slow release (Nuruzzaman et al. 2016). Nanomaterials are used both as active constituents or additives in the preparation of nanopesticides acting as protectants of crops (Khan and Rizvi 2017).

4 Nanoherbicides

Herbicides are chemical substances that are used to control or kill unwanted herbs or weeds. Herbicides work by physical or biochemical mechanism, that is, by absorption into the plants and translocation to the target site, disrupting the metabolic processes of weeds leading to weed death. Nanoherbicides are used as an effective approach to get rid of weeds. Lower quantity of herbicide is needed when active ingredients are combined with smart nano-delivery system. The growth of weeds, that had developed resistance to conventional herbicides, gets halted when the particles of soil blend with nanoherbicides. The nanoherbicides when blended with soil particles halt the growth of weeds that had become resistant to conventional herbicides (Ali et al. 2018). For controlling parasitic plants, nanoencapsulation approach can be very useful in withstanding the phytotoxicity problems associated with conventional herbicides used for treating parasites on the plant. As the nanocapsules reach the parasitic weed, the herbicide is delivered. Thus, lower doses of herbicides such as imidazolinones and glyphosate are required as they are degraded by the plant and gradually accumulate inside the weed leading to sink effect. Additionally, such nanocapsules are synthesized to enhance penetration through cuticle and leaves. Moreover, polymeric nanoparticles can be functionalized with different substances such as adjuvants (surfactants and oil substances), giving excellent penetration through the cuticle (Alejandro and Rubiales 2009).

5 Nanoinsecticides

The invention of nanoinsecticides is considered as one of the best alternatives to conventional insecticides that has broadened up the application arena of inorganic dusts. Polymeric nanoparticles are one of the mainstream nanostructure systems for efficient delivery of drug formulations. Most common shapes of polymeric nanoparticles for nanoinsecticides include electrospun nanofibers, nanogels, micelles, nanospheres, and nanocapsules (Sun et al. 2020). Table 1 shows some of the nano-based formulations against insects in comparison to conventional formulations.

Pheromones are one of the ecofriendly biological control agents and when conjugated with nanogels lead to higher efficacy. Environmentally safe management of fruit flies involving pheromones for lowering of pest attacks has been researched. Nanogels consisting of methyl eugenol pheromone have been reported to give stability at different environmental conditions in the orchards. This combination requires easy handling and lesser quantity of pheromone. Such nanopheromones are technically used to trap the pests found in orchards of guava and mango (Khan and Rizvi 2017).

6 Nanosensors

Nanosensors, also called nanobiosensors, give information about the pathogen and its location in real time (Baeumner 2004) (Stephen Inbaraj and Chen 2016). These are also used for the recognition of microbial environment, pollutants, pesticides,

Table 1 Efficacy of nanoinsecticides as compared to conventional insecticides (Sun et al. 2020)

Nanostructure	Polymers	Active ingredients	Target	Efficacy
Nanogel	Chitosan and cashew gum	*Lippia sidoides* essential oil	Aegypti larvae	Over 90% mortality rate even at low concentrations (48 ppm)
Nanosphere	Polyethylene glycol (PEG) and chitosan	*Geranium maculatum* and *Citrus bergamia* essential oils	*Culex pipiens*	1.61 and 2.53-fold acute larvicidal activity of PEG nanoparticles and chitosan nanoparticles, respectively, as compared to essential oil alone
Nanocapsule	Carboxy methyl chitosan and Azidobenzaldehyde	Methomyl	Armyworm larvae	5 days longer control period as compared to non-formulated active ingredient
Micelle	Polyethylene glycol (PEG)	Diethylphenylacetamide	*Culex tritaeniorhynchus*	80% more efficient at LC50
Electrospun nanofiber	Polylactic acid (PLA)/cellulose nanocrystal	Thiamethoxam	White flies	Efficiency at 50% of recommended dosage over 9 days

and for the determination of food freshness (Malhotra and Ali 2017). This information is valuable for the protection of crops from viruses, pathogens, and pests as well as for the enhancement of yield by providing suitable nutrients (Momin et al. 2013). In comparison with the conventional methods, they offer momentous enhancement in selectivity and sensitivity, and have enormous applications in agriculture and food (Chen and Yada 2011). The metallic nanoparticles like silver (Ag), gold (Au), CNTs, iron (Fe), nickel (Ni), and cobalt (Co) are utilized as nanosensors. Fluorescent probes of silica (SiO_2) nanoparticles have been used for the detection of a plant pathogen *Xanthomonas axonopodis*, which is responsible for the bacterial spot disease in plants of Solanaceae family (Yao et al. 2009). Carbon (C) nanoparticles are utilized for the detection of residues of pesticides in plants by means of their chemical sensing property (Sharon and Sharon 2008). The advancements in the preparation of some nanosensors are corresponded with the applications in food and agribusiness areas (Rai et al. 2012).

7 Nutrients Delivery

In agriculture and food sector, cumulative consideration is paid to the advantageous effects of nanoparticles employed in low dosages in crops, for instance, improved biosynthesis of secondary metabolites, enhanced antioxidant activity (Syu et al. 2014), more viable retention of water and fertilizers (Ghorbanpour and Hadian 2015), and so forth, which eventually results in increased plant growth and yield bringing financial benefit. Nanoparticles could be utilized as nanofertilizers for soil or as enriched delivery vehicles to enhance their uptake and also the functioning of traditional fertilizers (Liu and Lal 2015). Moreover, the lower rate of delivery of nanofertilizers keeps up the soil fertility by diminishing the movement of these fertilizers into a spillover or ground water and lessening the dangers of ecological contamination. Hydroxyapatite nanoparticles utilized as nanofertilizers of phosphorous (P) upgrade the seed yield and rate of growth of soybean as compared to the standard P fertilizer by 20% and 33%, respectively (Liu and Lal 2015). Metallic or metallic oxide nanoparticles such as copper (Cu), zinc oxide (ZnO), iron oxide (FeO), and titanium dioxide (TiO_2) might be employed as nanofertilizers when present in soil or via foliar application of these nanofertilizers in different crop plants, for example, spinach, mungbean, millet, and cucumber (Gao et al. 2006; Tarafdar et al. 2014; Verma et al. 2018). Recently, chitosan nanoparticles have been harnessed for the release of nutrients in a controlled manner. Such nutrients include potassium (K), phosphorus (P), and nitrogen (N) that are taken up by foliar means in wheat (Abdel-Aziz et al. 2016).

8 Seed Germination, Plant Growth and Development, Secondary Metabolism

Seed germination has been described as a critical phase in the plants' life cycle that encourages the development and survival of seedlings. For this, several studies have indicated that the use of nanomaterials positively affect germination of seeds and also growth and development of plants. For instance, zeolite, TiO_2, and SiO_2 nanoparticles stimulate germination of seeds in plants (Manjaiah et al. 2018). In spite of a critical research on nanomaterials, the primary mechanisms of how nanoparticles might activate germination are still ambiguous. Some studies have exhibited that nanoparticles can possibly absorb into the seed coat using water that activate enzymes, and eventually improve seed germination and seedling growth (Banerjee and Kole 2016). Along with germination, nanoparticles like TiO_2, multiwalled carbon nanotubes (MWCNTs), ZnFeCu-oxide, ZnO, FeO, and hydroxyl fullerenes have been reported to enhance growth and development of different crops including wheat, peanut, onion, soybean, potato, spinach, tomato, and mustard (Shalaby et al. 2016; Shojaei et al. 2018). Additionally, Fe/SiO_2 hybrid nanomaterials improve seed germination and plant growth in grains and maize (Najafi Disfani et al. 2017). Disfani et al. revealed that the shoot length of maize and barley seedlings is enhanced by about 20.8% and 8.25%, respectively, using 15 mg kg^{-1} of Fe/SiO_2 nanoparticles. However, the shoot length was adversely influenced when the dose was increased up to 25 mg kg^{-1}. Hence it was concluded that plant development relies upon the dose of nanoparticles. Moreover, fullerenes have been reported to upgrade hypocotyl development in *Arabidopsis thaliana* by an incitement of cell division (Gao et al. 2011). It has additionally been discovered that the dressing of seeds with fullerol results in increase in number and size of fruits as well as stimulation of bioactive compounds' formation such as lycopene, inulin, and cucurbitacin-B in *Momordica charantia* (Kole et al. 2013).

Elfeky et al. (2013) indicated that the plant development is also affected by the method used for nanomaterials' application. It was elucidated that the foliar use of Fe_3O_4 nanoparticles improved total chlorophyll, essential oil, carbohydrates, and Fe content along with the stature, leaves, branches, and fresh and dry weight of *Ocimum basilicum* contrasted with that of soil application (Elfeky et al. 2013). Nano priming is another strategy for the preparation of seeds with nanoparticles; for example, there is a study elucidating the stimulatory or inhibitory impact of nano-sized iron (Fe) and copper (Cu) on wheat (Nalci et al. 2019). According to this study, the germination rate, and root and shoot length were upgraded with Fe nanoparticles while Cu nanoparticles demonstrated inhibitory effect on development. Effect of Ag nanoparticles was investigated on wheat, barley, corn, watermelon (Almutairi and Alharbi 2015), and fenugreek (Hojjat and Hojjat 2015) seeds. Similarly, potential influence of CuO nanoparticles was evaluated on the seed germination and callus induction of fenugreek by Ain et al. (2017). There was increment in percent germination, seedling development, shoot length, chlorophyll content, and antioxidant production. However, decline in root length and biomass was observed at higher doses. Henceforth, it was concluded that there should be standardized dose of nanoparticles for each crop. Moreover, TiO_2-nanoparticle-coated seeds of fenugreek indicated an expansion in biochemical compounds such as carbohydrates, proteins, and chlorophyll as compared to control. This also prompted improved photosynthesis and metabolism of nitrogen, eventually improving seedling development (Missaoui et al. 2017). The influence of zinc oxide (ZnO) nanoparticles and chelated mass zinc sulfate ($ZnSO_4$) on peanut seeds was determined. It was seen that the dose of 1000 ppm of ZnO nanoparticles improved development as compared to chelated bulk $ZnSO_4$ by advancing seed germination and growth, chlorophyll content, flowering, root and shoot length, and pod yield per plant, but higher concentration of 2000 ppm had negative impact on these parameters (Prasad et al. 2012).

Various nanoparticles have been found to be beneficial for medicinal plants regarding their secondary metabolite production, antioxidant activities, and growth and development (Javed et al. 2017a, 2022b). Hence, nanoparticles have immense potential to act both as fertilizers and elicitors for bioactive compounds' production in bioreactors. For example, Javed et al. (2017b, c, 2018) reported enhanced physiology and biochemistry of *Stevia rebaudiana* micropropagated shoots and calli grown in the presence of ZnO and CuO nanoparticles. Ahmad et al. (2020) indicated the elicitation of morphological and biochemical parameters of tissue-culture-raised regenerants of *Stevia rebaudiana* using engineered ZnO and CuO nanoparticles. In addition, Elhaj Baddar and Unrine (2018) observed enhanced growth of wheat seedlings on exposure of ZnO nanoparticles. Similarly, Mosavat et al. (2019) documented the increment in growth of callus and its production of secondary metabolites in *Zataria multiflora* and *Thymus* species in vitro raised in the presence of nano ZnO. Sadak (2019) reported the increase in plant growth and biochemical aspects of *Trigonella foenum-graecum* using Ag nanoparticles.

9 Genetic Transformation

The cell wall of plants prevents any exogenous biomolecules from entrance into the cells. Genetic transformation is the way to move genetic material (deoxyribonucleic acid [DNA]) into plant cells that is usually performed by means of *Agrobacterium tumefaciens* or biolistic gene gun. The major obstacles to these procedures are limited host range and significant destruction of plant cells leading to impairment of growth and development. The vast majority of innovative investigations regarding genetic engineering assisted via nanomaterials have been carried out utilizing plant cell cultures in the past decade. For example, DNA has been effectively conveyed to different plant calli using silicon carbide (SiC)-mediated transformation (tobacco, maize, rice, soybean, and cotton) (Petolino and Arnold 2009; Asad and Arsh 2011; Asad et al. 2008). The simplified mechanism of plant genetic transformation using nanoparticles has been demonstrated in Fig. 2.

One pivotal investigation demonstrated that the double-stranded ribonucleic acids (dsRNAs) could be stacked on non-toxic and biodegradable layered double

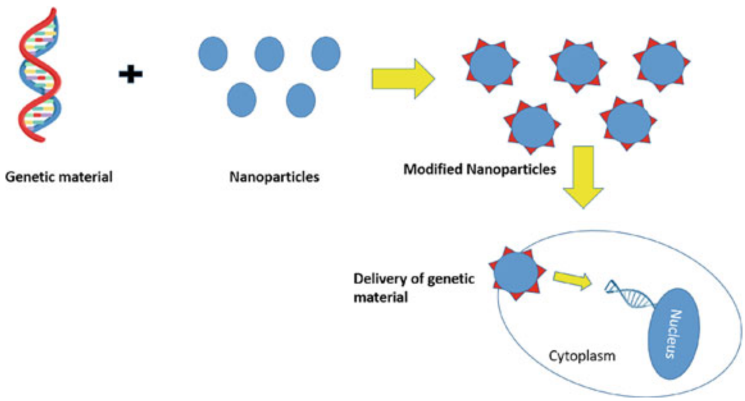

Fig. 2 Process of nanoparticles-mediated plant genetic transformation

hydroxide (LDH) clay nanosheets or BioClay. The beneficial aspect of dsRNAs or the products of the RNA breakage lies in their defensive behavior against cauliflower mosaic virus (CMV) found in the leaves of tobacco (Mitter et al. 2017). In addition, magnetic nanoparticles (MNPs) have been documented to induce a genetic change in cotton plants. The complex formed by the MNPs and β-glucuronidase (GUS: a reporter gene) invades into the cotton pollen grains by applying a magnetic force, without changing the viability of pollen. Owing to pollination with MNPs complex, an effective production of transgenic plants takes place by means of efficacious incorporation of exogenous DNA in the recipient genome. This foreign DNA is viably expressed and its stable inheritance occurs in the progeny attained by selfing (Wang et al. 2016). In another study, CNT scaffolds applied to the external tissues of plant by infusion have been utilized to supply linear and plasmid DNA along with the small interfering RNAs (siRNAs) in the leaves of *Triticum aestivum*, *Gossypium hirsutum*, *Nicotiana benthamiana*, and medicinal plant, *Eruca sativa*. Recently, genome editing has been proposed using mesoporous silica nanoparticles (MSNs). The MSNs are carriers for the transfer of Cre recombinase in the embryos of *Zea mays* and are involved in the conveyance of loxP sites of chromosomal DNA. In plant tissues, engineered MSN is induced by the biolistic strategy that accurately recombines the loxP sequence, hence making the genome editing successful (Martin-Ortigosa et al. 2014, 2012). Besides, the study by Mitter and colleagues has opened a way for the conveyance of RNA interference (RNAi) in plants utilizing nanomaterials (Mitter et al. 2017).

Fluorescence-labeled starch nanoparticles have also been utilized to convey DNA in plant cells. Starch nanoparticles loaded with DNA are cultured with the suspension cells of *Dioscorea* species that are then treated with ultrasound vibrations. Fluorescence label is utilized to follow the nanoparticle transport in the plant cells. The size of the DNA–starch nanoparticle complex extends from 50 to 100 nm and its entrance inside the cell is speculated through the pore produced by an ultrasound vibration (Liu et al. 2008). When complexed with starch nanoparticles, DNA is shielded from ultrasound impairment just as from DNase I cleavage. However, due to low transformation proficiency, starch nanoparticles are not much famous for DNA conveyance in plants (Le Corre and Angellier-Coussy 2014). Additionally, the gene transfer based on calcium phosphate (CaP) nanoparticles has been attained elucidating about 80% of transformation proficiency contrasted with ~54% via *Agrobacterium tumefaciens* (Naqvi et al. 2012). Among these nanoparticle-based procedures, silicon carbide (SiC)-facilitated DNA conveyance is an auspicious method to facilitate nucleic acid transfer in plant cells and has opened the way for non-traditional materials to convey biomolecules to the plant cells (Asad and Arsh 2011). In recent times, SiC whiskers are being utilized in peanuts to transform with the gene coding for chitinase. The transgenic plants obtained in this way demonstrate protection from leaf spot disease (Ul Hassan et al. 2016).

10 Antimicrobial Properties

Nanomaterials used as antibacterial and antifungal agents are of significant importance. The physiochemical properties that affect the antimicrobial activity of nanoparticles include size and structure, coating, chemical modifications, and solvents used (Gatoo et al. 2014). The nanoparticles of ZnO prevent the growth of *Staphylococcus aureus*, Ag nanoparticles display a dose-dependent antibacterial activity against *Pseudomonas aeruginosa* and *Escherichia coli* (Ramalingam et al. 2016), and TiO_2 nanoparticles have found the ability to attach with the surface of bacteria and produce reactive oxygen species (ROS), and cause damage to the structure of membrane that ultimately results in the leakage of cellular contents, and thus death of bacteria (Foster et al. 2011). Moreover, nanoparticles of Fe cause decomposition of the bacterial cell resulting in deactivation (Sultana et al. 2012). Tu et al. (2013) investigated the graphene nanosheets and their antibacterial molecular mechanisms against *E. coli*. Researchers have reached to the conclusion that phospholipids' isolation from the cell membrane occurs with the help of graphene nanosheets leading to the inactivation of bacterial cells (Tu et al. 2013). The nanoparticles of Al_2O_3 have been reported to trigger the pore formation in the bacterial cellular membrane that leads toward the loss of parent molecules, cell membrane destruction, and leakage to cytoplasm (Ansari et al. 2014). Nanoparticles of CuO act similar to other metallic oxide nanoparticles and disrupt the cell membrane along with the production of ROS; for example, *Bacillus anthracis* and *Bacillus subtilis* are both found quite sensitive to CuO nanoparticles (Gao et al. 2014).

11 Antioxidant Properties

Antioxidants are compounds that can safely interfere with free radicals and convert them to the non-toxic particles by giving an electron (Lobo et al. 2010). Recently, antioxidants have attracted much attention because of their capability to limit oxidative stress caused by the irregularity between oxidant production and the antioxidants to neutralize. Henceforth, there is a net increment of the ROS and reactive nitrogen species (RNS) (Gupta et al. 2015). ROS and RNS are involved in causing impairment to cell membranes, subcellular organelles, DNA, proteins, and lipids, consequently damaging the cellular function (Sharpe et al. 2011). Hence, oxidative stress appears to play a role in causing several diseases and injuries. Nearly all organisms have endogenous defense of antioxidants and repair mechanisms for safeguarding against oxidative stress. But these systems are often insufficient to totally forestall the damage (Bagchi et al. 2014). Therefore, the utilization of supplements of antioxidants is prescribed to diminish the oxidative impairment. Mostly, antioxidants employ their action primarily by two fundamental ways; either by averting the ROS/RNS development or by neutralizing it. Sometimes, enzymatic antioxidant compounds show activity by breaking down the ROS/RNS into neutral or less toxic products (Pellegrini et al. 2003).

Nanotechnology advancement has disclosed some nanoparticles either from biological (Liu et al. 2017) or chemical (Watanabe et al. 2009) origin as effective antioxidants. Metallic nanoparticles (Ag, Au, Pt) and metallic oxide nanoparticles (ZnO, CuO, FeO, NiO) are mostly utilized and assessed for their antioxidant potential (Patlolla et al. 2015; Saikia et al. 2010; Jadhav et al. 2018). Nonetheless, the antioxidant capacity of these nanoparticles relies upon their origin, surface charge, size, composition, and surface area to volume ratio (Shah et al. 2017). Furthermore, nanoparticles offer many benefits over conventional methods of antioxidants' delivery, which include enhanced bioavailability, biodegradability, and targeted and controlled release.

12 Food Processing, Packaging, and Transportation

Nanotechnology has gained enormous importance in all perspectives of food processing, packaging, and transportation. Various nano-food items are being developed. Active ingredients like fatty acids and vitamins encapsulated in nanoparticles are now commercially sold for usage in preservations and processing of meat, beverages, and other foods. A German company markets NovaSol containing nanotechnology-based carrier system utilizing micelles of 30 nm to encapsulate fatty acids and active ingredients of vitamins C and E utilized as preservatives. Aluminosilicate nanoparticles are normally utilized as anticaking agents in the processed food (Yada et al. 2014). Anatase titanium dioxide nanoparticles are used for whitening of cheese and sauces foods (Baranowska-Wójcik et al. 2020).

Nanoencapsulation comprised of vitamins, probiotics, minerals, and antioxidants are used for dairy products, breads, cereals, and beverages (Assadpour and Mahdi Jafari 2019). Nu-Mega Driphorm utilizes omega-3 food additives microencapsulated in tuna fish oil that is utilized to fortify Australian bread (Eratte et al. 2017).

There are numerous organizations in the food business that are utilizing nanotechnology. A company NutraLease Ltd. has created novel nutraceutical carriers to be integrated in food system. Nutraceuticals like beta-carotenes, lycopene, and phytosterols encapsulated in the carriers are utilized for healthy foods, particularly to forestall the cholesterol accumulation (Yi et al. 2015; Riangjanapatee et al. 2013). Oilfresh company presented antioxidation product Oilfresh1000 using nanotechnology, a deep-frying device in restaurant. The benefits of this product are that it keeps the frying oil fresh for a considerably longer time and also permits to change to healthier vegetable oils. Its outcomes are crispier food, better taste, better consistency, lesser costs, and more noteworthy benefits to health and environment.

The most primitive application of nanotechnology considered in the food business commercially is in food packaging. The shelf life of the products can be increased by utilizing nanopackaging materials that can deliver antimicrobials that control moisture or air exchange with the surrounding (Duncan 2011; Sorrentino et al. 2007). Nanopackaging can prolong the shelf life of various products by delivering different antimicrobials, nutraceuticals, flavors, enzymes, and antioxidants (Cha and Chinnan 2004; Lacoste et al. 2005). Furthermore, edible coating on nanoscale has been recently developed that can be utilized in fruits, meat, vegetables, bakery items, cheese, and fast foods. These edible coatings function as delivery vehicles for flavor, enzymes, color, antioxidants, and anti-browning agents, and also increase the shelf life by providing barrier to air and moisture (Weiss et al. 2006). Biocides are released from the packaging in response to microbial growth or humidity (Larson and Klibanov 2013). Some packaging materials integrate nanomaterials like Ag or ZnO and other nanoparticles having antimicrobial properties where the packaging itself functions like an antimicrobial agent (Legood and Clarke 2006). Nanobiodegradable packaging is also an application of nanotechnology (Kumar et al. 2018).

13 Nanoremediation

Nanoremediation is the use of techniques and processes to clean up the environment using nanomaterials. In contemporary years, the use of engineered nanoparticles has gained significant attention as they promise their potential for environmental remediation. In addition to their potential to remediate contaminated soil, water, and air, they are also considered to be a cost-effective approach and the best alternative to conventional remediation techniques. These engineered nanomaterials exhibit their unique properties of high surface-to-volume ratio, high activity of atoms at surfaces, and increased magnetization values and quantum effects that make these nanomaterials one of the most exciting platforms for environmental remediation.

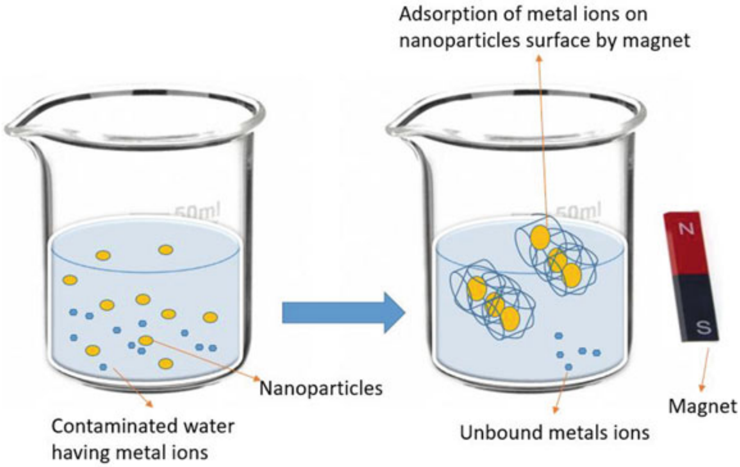

Fig. 3 Remediation of contaminated water using nanoparticles

Thus, nanoremediation can be shortly defined as "tiny particles cleaning up big environmental problems." Recently, 70 sites in the world have been evaluated to be treated using nanomaterials either at full scale or at pilot scale (Grieger et al. 2015).

In the last few decades, with budding industrial, agricultural, and urban activities, the magnitude of ground water pollution is reaching to a higher level. Untreated effluents are directly dumped into wells or other water sources that ultimately become the source of partial or complete loss of soil and ground water quality. In addition, manure and inorganic fertilizers (N and P) and pesticides are found to be the major causes of ground water contamination. Among the most detrimental compounds entering the ground water are due to the excessive use of fertilizers and pesticides in agriculture and illegal industrial activities releasing organophosphorus, organochlorines, and heavy metals in the environment (Ingle et al. 2014). The role played by nanoparticles in remediation of contaminated water has been illustrated in Fig. 3. For this, nanozerovalent iron ions (nZV1) are found to be one of the most widely studied chemicals for groundwater remediation (Grieger et al. 2010). nZV1 consists of a metallic core of iron and a thin oxide layer on the surface. The adsorption capacity is provided by the core to the contaminant surface. Most importantly, organic and inorganic coatings or surfactants mainly improve the quality of adsorption and reduction functions for contaminant removal.

Top soil applications are more acceptable as compared to traditional agricultural practices owing to the ability of disseminating nanoparticles to the contaminated zone (Pasinszki and Krebsz 2020). ZnO and TiO_2 nanoparticles are considered to be on the top of list of nanoparticles for their electronic-gas sensing as well as photocatalytic, energy converting, and semiconducting nature. Due to these properties, scientific community is working on these nanoparticles to treat waste water. Among many kinds of nanomaterials, metal and metal oxide nanoparticles are grabbing attention due to their separation assisted by magnetic field, which is crucial for nanoremediation (Ingle et al. 2014).

14 Nanotoxicology

Plants are among one of the most important components of ecosystem and are considered to be the most crucial ecological receptors having potent pathway systems for the bioaccumulation and transport of nanoparticles into the food chain. Adverse effect of nanoparticles can take place in different scenarios where they can cause damage to environment or endanger every sort of life, that is, plants, animals, and human health (Donaldson et al. 2004). Thus, for the last two decades, diverse applications of nanoparticles have led to the basis of nanotoxicology, which is a field of nanotechnology about the study of toxic effects of nanoparticles on natural environments. The major aim of nanotoxicology is to make guidelines for the safe fabrication of nanoparticles and their potential effects on body, organs, tissues, and cells (Jamil et al. 2018).

Generally, two major approaches are utilized for measuring the nanoparticles' toxicity; one is in vitro cell line experiments, and the other is in vivo model organism experiments using *Arabidopsis thaliana*. There is also a third approach, which is computer simulation, but it is not quite reliable for studying the pathways and toxic effects of a wide range of nanoparticles as it is impossible for a computer system to accurately analyze the interactions of various nanoparticles and living matter; thus computer simulation approach is not always considered for the study of nanotoxic effects (Sukhanova et al. 2018). In vitro studies largely evaluate the nanoparticle toxicity on different cellular levels. These effects can be in the form of oxidative stress, disturbance in growth and development, malformation, and mortality. Production of excessive ROS and free radicals causes inactivation of antioxidant defense system, DNA damage, and lipid peroxidation (Walters et al. 2016). Moreover, higher quantities of nanoparticles can alter the physio-morphological events of crops. Larger concentration of nanoparticles gathered around the roots can impede germination of seeds, halt the development of roots, alleviate the uptake of water and nutrients, reduce the growth of leaves, and mitigate the biomass production. Nanotoxicity results in oxidative outburst that disorganizes the chloroplast, disturbs photosynthesis, disrupts cell membrane, and hampers gene expression (Usman et al. 2020), as depicted in Fig. 4.

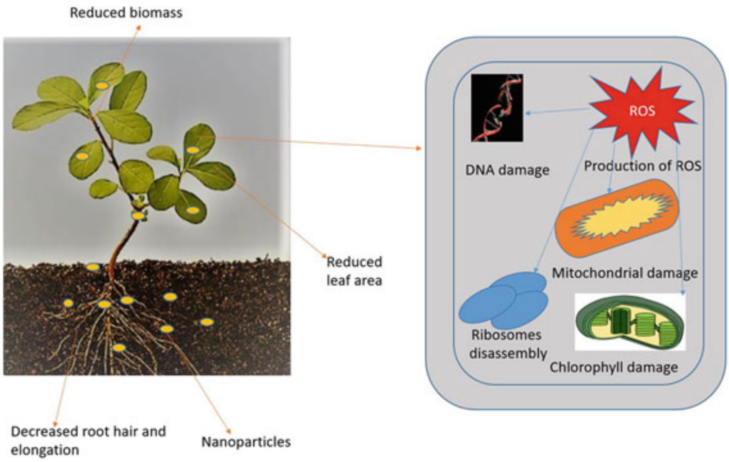

Fig. 4 Diagrammatic depiction of impacts of nanotoxicology on plants

15 Regulation and Legislation for Safety Concerns of Nanoparticles

About 60% population of the world is dependent on agriculture and agroindustry for its existence and survival (Ali et al. 2018). In the modern world, sustainable production of crops is impossible without the use of synthetic agrochemicals such as fertilizers, pesticides, and herbicides (Prasad et al. 2017). Nanotechnology is considered to be one of the "key enabling technologies" that plays its role in sustainable growth and development in agriculture sector due to the increased demand of food under climate change scenario across the globe. Leading analyses of research and development (R & D) sectors say that nanotechnology had been applied in the field of agriculture since a decade ago while looking for ways to combat global food insecurity challenges of greater crop productivity with improved produce quality, and sustainable and innovative environment-friendly cropping system. Many authors have reported that agri-nanotechnology has gained a growing trend of scientific publications and patents specifically for crop production and disease management (Jampílek and KráL'Ová 2015).

Government agencies are deliberately concerned about the regulation of many aspects of nanotechnology. Consuming nanotechnology in food and agriculture is one of the latest attention-grabbing topics, which was first put forward in 2003 by U.S. Department of Food and Agriculture. Countries in Europe as well as countries such as China, Japan, Iran, India, Thailand, and a number of other countries around the globe contributed their roles in providing legislation and safety guidelines. Different international organizations have prioritized regulations for the development of agri-nanomaterials. These organizations include Food and Agriculture Organization (FAO), the European Union (EU), Organization for Economic Co-operation and Development (OECD), and Australian Pesticides and Veterinary

Medicines Authority (APVMA). Different regulatory approaches are followed by OECD and non-OECD countries, and globally only Switzerland and the EU have properly established legislative frameworks for the use of nanomaterials in agriculture and food sector. Other non-EU countries have no proper legislative measures for employing nanomaterials in agriculture. In the EU, the main legislative body is REACH—Registration, Evaluation, Authorization and Restriction of Chemicals—which is concerned with nanomaterials' usage specifically in food additives, food supplements, food contact products, and plant protection agents (Mitter et al. 2017).

Nano-food markets around the globe including the big companies Unilever, Craft, Nestle, and Heinz have found nanotechnological applications for food packaging and processing. Greater percentage of food products contains organic and inorganic nanoparticles. In Europe, some inventors have announced a list of products with the claim of having nanoparticles in the food sold in the market. Some databases such as Nanodatabase, Consumer Product Inventory, BUND database, Nanotech data, Nanoproducts, and ANEC/BEUC are among the forefront databases in Europe that inform about the food product or packaging material containing nanoparticles inside (Tarhan 2020).

16 Public Awareness and Acceptance

Nanotechnology in agriculture is the dire need of today as globally millions of people need food and water to live. There is a ray of hope for alleviating hunger and poverty along with keeping away the potential risks associated with the use of nanotechnology. A study elucidating the moderate public opinion about nanotechnology and hope for acceptance of this field by the society has been documented by Kah et al. (2018). Survey done in the USA concluded that respondents think that nanomaterials are safe to use and less risky as compared to the genetically modified organisms (GMOs), pesticides, and chemical disinfectants. Despite the public acceptance, there is very little knowledge about the fate, passage, and performance of nanotechnological products. Unfortunately, greater mass of public is unaware of agriculture system and, most importantly, the brilliant minds in our society are still reluctant and not attracted toward agri-nanotechnology worldwide. Thus, proper guidance is immediately needed to create awareness among agriculture industry stakeholders on agri-nanomaterials and to attract brilliant learners (Mukhopadhyay 2014).

Public awareness and acceptance is one of the crucial steps while consuming nanotechnological products although this step is often neglected by the food manufacturers. This is most of the time due to the fact that manufacturers do not want to dispose their products to public due to the competition in business. This can be unfair to the public as they are deliberate to know about why and how the new product came to the market. Studies have shown that Ag nanoparticles were used in packaging due to their antimicrobial properties but at the same time, public was using these products being unaware of its packaging. This was both an unethical and illegal act. Therefore, proper labeling is needed to make the information transparent to the general public for using nanoparticles (He et al. 2019). A study done on public acceptance of agri-food suggested that the greater number of people were unaware of nanotechnology; perceptions were gender-based, and females and young people had more awareness of health-based nano-foods. They also had greater acceptance of welfare of nanotechnology (Mccarron 2016). Another survey done in Ireland was based on the interview of 14 agri-food stakeholders and online questionnaire filled by 88 stakeholders that resulted in a conclusion that the awareness about agri-nanotechnology in Ireland is low, and people of Ireland are neither positive nor negative regarding food applications of nanotechnology. Increased product shelf life, safe food, and low waste were considered to be the main agri-nanotechnological requirements of the people of Ireland.

17 Final Remarks and Future Perspectives

This chapter covers various applications of nanotechnology in the field of agriculture and in agroindustry. These applications involve the use of different nanoparticles such as nanofertilizers, nanopesticides, nanoherbicides, nanoinsecticides, nanosensors, nanoantimicrobials, and nanoantioxidants. Also, the employment of nanoparticles in nutrient delivery, seed germination, plant growth and development, metabolomics, genetic transformation, food processing, packaging and transport, and remediation of environmental pollutants/toxicants has been discussed. The major constraint of agri-nanotechnology includes marketing of nanoproducts due to the fear of nanotoxicity. To overcome this, agri-nanotechnology needs to be better advocated toward the public so that their awareness and acceptability of nanoproducts could be enhanced. Moreover, the regulatory and legislative policies should also try to neutralize the battle between the manufacturers and consumers of these products.

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Nanotechnology and Omics Approach in Agrobiotechnology

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1 Introduction

Agriculture is the strength of Indian financial system and provides plenty of food to assure the need of growing human residents. Application of crop protectants, fertilizers, and pesticides is beneficial to agriculture system; however, unsystematic pesticide use not only contaminates agriculture produce but also affects soil fertility and water quality which have an effect on human health (Kumar et al. 2021). Therefore, it is essential to improve soil fertility by new technology such as nanotechnology, which is concerned in growth and productivity of plants by means of recycling of essential nutrients via biogeochemical cycles (Chaudhary et al. 2021a). Nanotechnology term first time was given by Norio Taniguchi in 1974. It is an innovative and promising field of interdisciplinary studies. Nanoparticle (NP) (nanocrystal/nanopowder/nanocluster) can be defined as a microparticle in a range of nanometer (1–100 nm) (Bajpai et al. 2018). Due to their smaller size, they possess numerous properties, that is, uniformity, optical properties and/or conductance, which are otherwise absent in their large sized parent materials. Therefore,

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they are in great demand in agriculture to enhance crop production, food superiority (nanofertilizers), protect plants towards pathogens (nanopesticides) and help in scrutinize the soil quality and different stresses using nanosensors (Zulfiqar et al. 2019; Kah et al. 2019). Nanotechnology has various applications in plant productivity, including controlling nutrient release and assessing water quality for sustainable development of agriculture. Nanoformulations such as nanoclay, carbon nanotubes and hydroxyapatite help plants to grow and develop by delivering the nutrients (Rastogi et al. 2019). To keep soil fertile, it's also important to study the contact between NPs and microbial population of soil. Researchers have found that various concentrations of NPs have positive and negative impact on soil and plant health. Omics study is assigned for screening of biomolecules in an organism, particularly at genomics, transcriptomics, proteomics and metabolomics level. These techniques have been broadly used to analyse the uptake, bioaccumulation, alteration and jeopardies of NPs to different crops (Hossain et al. 2015). Advanced strategies to examine DNA and RNA from plant and soil permit us to recognize the microbial population associated to different surfaces. Metagenomics helps in quantify the soil microbial diversity under different environmental conditions and identify the novel genera, species as well as genes. Proteomic study has become a potent means for the recognition of stress-induced proteins and creates the intrinsic information of plant stress towards NPs exposure. Liquid chromatograpgy mass spectrometry (LC-MS) and Gas chromatography mass spectrometry (GC-MS) permit the qualitative and quantitative estimation of the metabolites of plants and soil rhizosphere (Zhang et al. 2012). Metabolomics is a powerful tool that helps in analysis of different metabolites, which are the products of gene expression and minor variations in protein and gene level (Kusano et al. 2011). It helps in determination of amounts of sugar, lipids, organic acids, steroids and nucleotides from different samples. Multiomics technology helps in solving different problems related to plant defence response, stress conditions to know the microbial flora of soil at different sites (Sarrocco et al. 2020).

2 Different NPs in Agriculture Practices for Improvement in Plant Growth and Soil Heath Under Different Conditions

Plants are important part of the food chain since they are eaten by animals; NPs may be transferred to them; their fate and transport in the ecosystem are determined by them. The NPs morphology, functional group type, coating, and concentration all affect how well plants can absorb them. Due to their nanosize and unique chemical and physical properties, engineered nanomaterials (ENMs) are developed and expanded for agriculture applications. NPs cover a variable array of materials and play dynamic role in crop growth (Agri et al. 2021). NPs are beneficial and may be toxic at the same time. Different plant species acted contrarily to similar category of

NPs of dissimilar size and concentration. A nanoparticle leads to changes in plants at physiological, morphological and genetic level. However, to know the application of nanoparticle in agriculture, it is vital to know the role of different nanoparticles on plant health and productivity as well as their soil microbial diversity. Wheat crop was found to benefit from nanochitosan, which greatly improved seed germination (Li et al. 2018). AgNPs significantly increased the leaf number, root/shoot length and diosgenin level in fenugreek plants reported by Rastogi et al. (2019). Beneficial effect of TiO_2 NPs has been observed in plant growth development under salinity stress by increment of stress enzyme activities, accumulation of sugars and proline (Gohari et al. 2020). Tymoszuk and Wojnarowicz (2020) reported that low ZnO NPs concentrations rouse the germination in seeds of *Allium cepa*. Kornarzyński et al. (2020) observed the positive effect of Fe_2O_3 NPs in seed germination of *Helianthus annuus*.

Positive impact of gold NPs in *Mimusops laurifolia* in terms of both number and size of the leaves was observed (Alshehddi and Bokhari 2020). Application of nanochitosan (50 mg L^{-1}) enhanced seed germination, agronomical/biochemical parameters and yield of maize (Chaudhary et al. 2021c). Plaksenkova et al. (2020) observed that zinc oxide NPs enhanced seed germination and plant height in barley. TiO_2 NPs improved the biochemical parameters of Moldavian balm plants under salinity stress (Gohari et al. 2020). SiO_2 nanoparticles (300 ug/L) improved the growth of sugarcane under chilling stress by enhancing the photosynthesis and photoprotection mechanism (Elsheery et al. 2020). Tauseef et al. (2021) found that MgO NPs (0, 25 and 50 ppm) improved the growth of cowpea and biochemical attributes. Application of nanochitosan (10 mg/L) induced microspore embryogenesis and plantlet development in rapeseed (Ahmadi and Shariatpanahi 2015). Zhang et al. (2019a, b) found that SiO_2 NPs under phosphorus deficiency enhanced stomatal conductance, antioxidant enzymes and water use efficacy. Chitosan NPs improved the agronomical and biochemical attributes in maize plants (Choudhary et al. 2017). ZnO NPs increase the growth of plants by increasing the zinc contents and improved the efficiency of nutrient uptake by plants (Wan et al. 2020). SiNPs enhanced the yield of wheat grains and reduced the accumulation of cadmium (Hussain et al. 2019).

Soil microbial activity is decisive for nutrient cycling and degradation of organic compounds. To establish that the soils hold healthy microbial population is essential from the perception of many disciplines (Sergaki et al. 2018). So, it is vital to know and measure the impact of different NPs on microorganisms so that soil health can be preserved. Application of agriusable nanocompounds such as nanozeolite and nanochitosan improved the soil enzyme activities and soil physicochemical parameters under maize and fenugreek cultivation (Khati et al. 2017, 2018; Kumari et al. 2020a, b). Positive effect of nanosilicon dioxide on maize and soil health was reported by Kukreti et al. (2020). Nanozeolite and nanogypsum were also involved in raising the growth and protein content in different beneficial bacterial isolates (Khati et al. 2019a; Chaudhary and Sharma 2019). Arbuscular mycorrhizal fungi with TiO_2 had positive impact on bean plants and enhanced chitin synthase genes in roots under salinity condition (Gohari et al. 2020). The bacterial and fungal

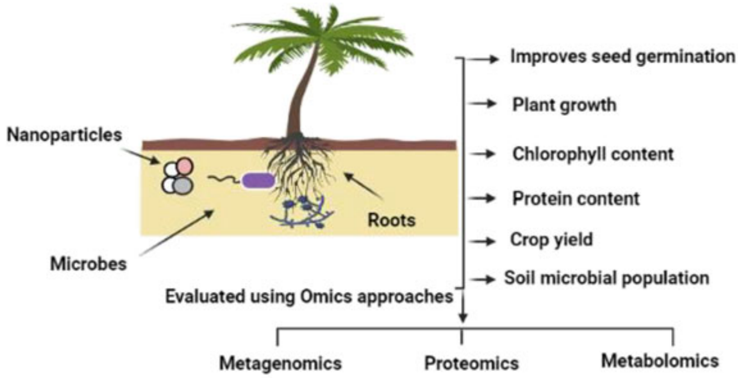

Fig. 1 Role of nanoparticles and omics approaches in agrobiotechnology

populations in alfalfa straw were improved by nanozeolite application (Aminiyan et al. 2018). Application of SiO_2 nanoparticles can encourage germination of seeds and antioxidant activity under salt stress in numerous crops (Siddiqui et al. 2014). Sillen et al. (2015) reported the effect of nanosilver (100 mg kg^{-1}) on U.S. Food and Drug Administration (FDA) activity of maize rhizosphere and found less FDA activity in treated soil. Silver NPs (1 mg kg^{-1}) declined the activity of dehydrogenase enzyme in the treated soil (McGee et al. 2017). Chai et al. (2015) found that metal oxide NPs improved the nitrogen and phosphorus solubilizing bacteria. Metch et al. (2018) observed some shifts in functional microbial community on exposure of gold nanoparticles. Zinc oxide NPs improved the soil dehydrogenase activity of soil reported by Kwak et al. (2017). Karunakaran et al. (2013) observed that SiO_2 NPs enhanced the soil nutrient content and proliferation of rhizobacterial population also supported the seed germination in maize (Fig. 1).

3 Metagenomics to Study Effect NPs on Soil Microbial Dynamics

Nitrogen, phosphorus and potassium solubilizing population and soil health were improved when nanogypsum (50 mg L^{-1}) applied on maize plants. Metagenomic study revealed the beneficial microbial improved under the influence of nanogypsum and nanozeolite which supported the abundance of *Proteobacteria* (Khati et al. 2019b; Chaudhary et al. 2021d). Bacterial phylum such as *Proteobacteria*, *Firmicutes* and *Actinomycetes* were enhanced under the influence of nanozeolite and nanochitosan (Chaudhary et al. 2021b). AgNPs also supported the *Proteobacteria* population reported by Chavan and Nandananthagam (2019). On the other hand, silica and magnesium NPs decrease the *Cyanobacteria* and *Proteobacteria* population (Shao et al. 2016). Application of silver nanoparticles (0.01 mg kg^{-1}) significantly reduced the population of ammonia oxidizers (–17%)

but have positive impact on the population of *Bacteroidetes* and *Actinobacteria* (Grün et al. 2019). Modified sulphated polystyrene NPs increased the rhizospheric bacterial counts reported by Kibbey and Strevett (2019). Abundance of *Chloroflexi* and *Planctomycetes* decreased significantly in maize rhizosphere when treated with silver NPs (10 mg/kg), but *Acidobacteria, Alphaproteobacteria* and *Bacteroidetes* were increased (Sillen et al. 2020). Luo et al. (2020) observed that CeO_2 and Cr_2O_3 NPs with CO_2 improved the abundance of *Bacteroidia* and *Gammaproteobacteria* and *Alphaproteobacteria*. Nanozero valent iron promoted the population of *Firmicutes, Acidobacteria* and *Proteobacteria* in Lufa 2.2 and 2.4 soils (Fajardoa et al. 2018). Application of silver NPs (0.01 mg/kg) increased the population of *Actinobacteria* and *Bacteroidetes* and decreased the ammonia oxidizers (Grün et al. 2018). Hydroxyapatite NPs influence the microbial community in soil in a complex manner (Cui et al. 2018). Silver NPs (660 mg kg^{-1}) decrease the population of *Rhizobium* in arctic soil (Kumar et al. 2014). Doolette et al. (2016) found that OTUs of amoA bacteria gene abundance are less sensitive towards the Ag_2S-NPs. Use of gold NPs as nanofertilizer reinforced the growth of numerous rhizospheric bacteria (Shukla et al. 2005). Some shifts in functional features of the microbial community structure were observed on exposure of gold nanoparticles (Metch et al. (2018). They reported higher population of *Actinobacteria, Chloroflexi* and *Bacteroidetes* in the treated soil. Application of nanozero valent iron increase the population of *Verrucomicrobia* abundance in Lufa soil (Fajardoa et al. 2018). Polystyrene NPs (10 mg L^{-1}) inhibited the nitrifying and denitrifying enzymes in constructed wetlands (Ma et al. 2021). Zhai et al. (2021) reported that TiO_2 NPs inhibited the *Verrucomicrobia* and *Acidobacterial* population in clay and sandy soils. Copper-based nanopesticides decreased the β-glucosidase activity in soil and significantly changed the bacterial and fungal population (Peixoto et al. 2021). Application of graphene and fullerene nanoparticles to soil increases the alpha diversity of bacterial communities, with populations of Actinobacteria and Chitinophagales greatly as compared to control (Wu et al. 2021). Exposure of nCuO (54–103 mg K^{-1}) increased the population of lignin degrading bacteria such as *Acinetobacter, Rhodanobacter* and *Sphingomonas* (Samarajeewa et al. 2020). Plant growth-promoting rhizobacteria (PGPR) such as *Pseudomonas fluorescens*, *P. putida*, *Bacillus subtilis*, *Paenibacillus elgii* when treated with Au, Al and Ag coated nanoparticles were found to not only considerably boost plant development but also prevent the growth of detrimental fungal parasites even within rhizosphere, making them potential nanofertilizer (Gouda et al. 2018).

4 Proteomics to Study the Plant and Soil Microbial Flora

There are a variety of crops which were exposed to different NPs and their impact was observed using proteomic approaches. AgNPs (15 nm) increased the root length and amino acid synthesis in soyabean crop under flooding condition (Mustafa et al. 2016). Hossain et al. (2015) found that Al_2O_3 maintained the soyabean growth like control and revealed that galactose oxidase and quinine reductase genes were upregulated in Al_2O_3 but ZnO and AgNPs affected the growth and downregulated the genes. When wheat was exposed to AgNPs, shoot and root length increased, and a proteomic analysis showed that proteins and genes related to photosynthesis were raised when compared to the control, but proteins related to glycolysis were decreased (Jhanzab et al. 2019). Soybean growth improved under flooding condition when treated with AgNPs and increased the proteins related to protein degradation (Hashimoto et al. 2020). Application of copper NPs in wheat crop not only increases the number of proteins involved in glycolysis and Tricarboxylic acid cycle (TCA) cycle but also decreases the tetrapyrrole synthesis related proteins (Yasmeen et al. 2016). *Pseudomonas aeruginosa* expressed (23–40%) total transcript when treated with silver NPs which was involved in denitrification process (Singh et al. 2019). Khodavaskaya et al. (2013) observed that carbon nanotubes NPs upregulated different genes which were involved in stress responses, signal transduction, metabolic and biosynthetic process in tomato leaves. Mitogen-activated protein kinases also upregulated which involved in plant cell growth and division. Mirzajani et al. (2014) observed that exposure of silver NPs on *Oryza sativa* crop regulated the genes involved in oxidative stress tolerance, transcription and calcium regulation. Application of iron oxide NPs improved the protein and photosynthetic metabolism-related proteins (Yasmeen et al. 2016). Alteration in proteins involved in sulphur metabolism was observed in *Eruca sativa* when exposed to silver NPs (Vannini et al. 2013).

5 Metabolomics to Study the Plant and Soil Microbial Flora

Metabolomics study not only provides the information regarding the metabolites under usual and stress conditions but also helps in determination the taxological and positive impact of NPs. The positive effect of iron oxide NPs on maize roots and antioxidant defence response were inactivated showed the protecting role of NPs for soil microns and roots (Yan et al. 2020). TiO_2 NPs significantly reduced the rice biomass but formation of secondary metabolites and amino acids increased in treated samples over control estimated using GC-MS metabolomic analysis (Wu et al. 2017). GC-MS analysis of *Arabidopsis* leaf extract revealed that organic acid compounds detected which protect plants from pathogens under the influence of NPs (Kumari et al. 2020a, b). Zhao et al. (2019) observed that NPs significantly increased the linolenic, hydroxycinnamic acid and allo-inositol in roots and leaves of maize plants. Li et al. (2021) revealed that application of ZnO and SiO_2 induced the changes in metabolome of cucumber leaves and up and downregulated the amino acids, sugars and secondary metabolites. CeO_2 NPs (0–500 mg kg^{-1}) application on wheat plants showed the induction of 180 metabolites using metabolomics study which play important role in iron storage in grains (Rico et al. 2020). CeO_2 NPs downregulated the expression of amino acids such as methionine, aspartic acid, tyrosine and glutamic acid in spinach plants (Zhang et al. 2019a, b). Silver NPs prevent the growth of *Alternaria blight* which causes disease in plants by increasing the activity of polyphenol oxidase estimated by metabolome analysis (Mahawar et al. 2020). Iron oxide NPs enhanced seed germination and oxidation of NPs inside plants with any toxic effect on soil and plant revealed using Inductively coupled plasma mass spectrometry (ICP-MS) (Das et al. 2016). Increment in concentration of sterols such as stigmasterol and campesterol was observed in silver NPs treated plants detected using GC-MS analysis which provides protection to plants from pathogens (Moghaddam and Ende 2012). Level of glutamic acid precursors was enhanced when maize plants are grown in NPs treated soil which play an important role in plant growth and development. Different metabolites such as levoglucosan, sugars, amino acids and amides in maize plant roots were observed under the influence of NPs by GC-MS (Zhao et al. 2019).

6 Conclusion

Sustainable advancement in agricultural production requires integrative tactics to meet rising burden and maximize source optimization. Nanotechnology has confirmed well-built prospective to support plant growth and protection towards biotic/ abiotic stresses. In addition, it also helps in improvement in soil microbial flora which supports plant productivity and health. Omics techniques have highly developed our perceptive of plant–microbe and nanoparticles interactions in numerous ways and will become the conventional approach to quickly identify the genes and enzymes responsible to plant growth and development. This will foster success in the development of different crops for sustainable agriculture. By using advanced techniques, different novel species are identified which tell about the impact of different NPs either positive/negative to that particular site. In order to accurately assess the impact of NPs on plants and soil, a widespread omics approach is also required.

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Interactions Between Nanomaterials and Plant–Microbe Partnership

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1 Introduction

The current agronomy based on monocrops is focused on maintaining them healthy against biological invasions from pathogens such as pests and weeds, which reduce their performance from 10% to 40% leading to annual economic losses of up to $248 billion in global agriculture (Lo Presti et al. 2015; Fried et al. 2017). The effects of the rhizosphere microbial community on plant growth and health were studied so far last years to understand the interaction between plants and soil. However, this task gets complicated when other factors are considered, like the influence of microorganisms and insects, which are also part of the biological system. Plants, microbes, and insects adopt different communication strategies to influence each other that could cause favorable conditions for all the parties or induce adverse effects to others as a defense mechanism. These communication strategies may include molecular physiology and biochemistry changes in plants strongly associated with the production of volatile and non-volatile compounds, metabolites, or even visual signals for insects (Franco et al. 2017; Islam et al. 2018; Tölke et al. 2020).

Nowadays, nanotechnology appears to be a practical solution for creating crops with a higher nutrient content by modifying metabolic routes and defense products that can act against disease generator pathogens. Although some researchers speak of nanotechnology as the future approach for advanced agriculture, it is essential to know all nanomaterials' (NMs) action mechanisms. It is known that those materials can be beneficial to specific organisms and detrimental to others. These could lead to

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an ecotoxicological issue relating to nanoparticles' use and their fate when interacting with several organisms (Dimkpa 2018; Banerjee and Kole 2016).

Organic matter is composed of various chemical compounds, such as organic acids, that can interact with nanoparticles affecting their surface properties, making their interaction a much more complex system (Dimkpa 2018; Du et al. 2018).

The main goal of this chapter is to review and provide a walkthrough to the reader on the state-of-the-art of fundamental interactions among plants, microorganism, insects, and soil when interacting with nanoparticles for crop development improvement, disease prevention, pest control, as well as beneficial and detrimental interaction with crop-related organisms.

2 Plants and Microbe Environments

The development of plants is a complex mechanism regulated by many factors, such as the environmental conditions present, the bioavailability of nutrients, the plant's characteristics, and the vast presence of microorganisms (bacteria and fungi) that inhibit the substrates. The roots form the primary organ through which most interactions with the microbiota present in the soil are carried out (Saleem et al. 2018). Plants benefit from bacteria and fungi, being an essential part of their development (Pii et al. 2015). The region in which the roots and the bacteria are present and interact is known as the rhizosphere. In the rhizosphere, bacteria and fungi carry out processes that help crops develop, such as the easier absorption of micronutrients present in the soil (Kumar and Dubey 2020).

The study of the interactions present in the rhizosphere is a subject that continues to be developed to reveal mechanisms that can be used to improve the health, productivity, and development of various crops (Dessaux et al. 2016; Hassan et al. 2019; Xiong et al. 2020; de Vries et al. 2020; Qu et al. 2020; Brunel et al. 2020).

Among the main functions carried out by the microbiota present in the substrate in interaction with the plants (as shown in Fig. 1), the facilitated acquisition of micronutrients, such as iron, nitrogen, potassium, and phosphorus as well as other essential micronutrients, the production of phytohormones which promote plant growth (Spaepen 2015), the increase of tolerance against abiotic stresses (high/low temperatures, salinity, and heavy metals), and indirect protection to pathogens that affect the development of a plant (Schlaeppi and Bulgarelli 2014).

Root exudates mainly influence plant interaction with soil bacteria; these compounds with different structures like organic acid, carbohydrates, metabolites, and amino acids can alter certain bacteria strains. In some scenarios, plants can produce a specific type of exudate to increase the number of existing bacteria in the soil and increase the benefits.

Exudates are also crucial for balancing pH soil and affecting ions' bioavailability (Haldar and Sengupta 2015). However, plant exudates serve to attract growth-promoting bacteria, but the presence of disease also causing bacteria can be

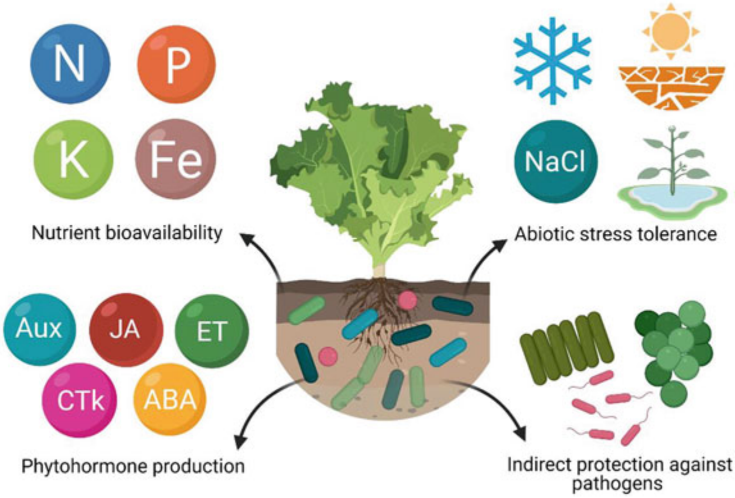

Fig. 1 Beneficial effect caused by the interactions between plants and microorganisms present in soil (created by Biorender.com)

modulated by some plant exudates, serving as repellants reducing the presence of detrimental species for development.

Plant growth-promoting bacteria (PGPB) serve as microorganisms that cope with plants and help in many processes in plant development. They can be found in the rhizosphere region, within the plant tissues, root nodules, or present in the soil without being in direct contact or attached to the plants. Even though PGPB can be distributed in multiple regions, they are still part of the fixation process of elements like nitrogen, carbon, sulfur, and phosphorus (Ambreetha and Balachandar 2019; Kumar et al. 2019).

A large variety of bacterial strains are present in the soil and can induce a best number of effects that can benefit plant health. Some examples include *Azospirillum* which main features are helping vegetables to fix nitrogen (N_2), phosphate solubilization, enhanced water and micronutrient uptake (Cassán et al. 2020) as well as the production of phytohormones for plant growth, including the capability of protecting the plants against biotic and abiotic stresses (Fukami et al. 2018). The genus *Pseudomonas* also has an interest in plant protection due to the antagonist role toward disease-causing bacteria to prevent diseases like bacterial speck, canker, wilt, stem root, root knot, among others (Singh et al. 2017).

PGPB can also help the plant withstand the stress caused by the heavy metal presence in the soil, as shown by (You et al. 2021), where soybean inoculated with *Burkholderia contaminans* ZCC shows resistance toward Cd (II). Potato plants isolated with *B. phytofirmans* show higher shoot and root growth with an enhance of salicylic acid present in roots in the shoot as well as an increase of absinic, salicylic, and jasmonic acids, where the increase of the presence of hormones is related to the effect of plant growth promotion observed by (Kurepin et al. 2015).

Knowing that microorganisms are beneficial to plant development and contribute to several mechanisms that increase micronutrient uptake and abiotic stress tolerance, they become essential for today and future crop development techniques to assure products with higher benefits (Pii et al. 2015).

Plant disease-causing bacteria lead to great losses in crop yield. For example, a significant amount of crop losses has been observed of rice of up to 60% due to *Xanthomonas oryzae pv. oryzae*'s infections (Jain et al. 2020). Nowadays, this problem is solved with the usage of pesticides that mainly may cause harm to humans. The global need to face plant diseases, but considering environmental restrictions, has stated new research paths to get eco-friendly and sustainable techniques. Thus, researchers in this area have been focused on understanding the communication between microorganisms and plants and vice versa.

Latest research shows that these interactions occur through the secretions of microorganisms which mainly stimulate the plant hormonal system. Also, in some scenarios, a defense mechanism is being activated, and its attributes related to plant growth are being affected by secreting some chelated compounds that plants absorb as nutrients. In general, symbiotic and pathogenic microorganisms establish communication channels based on secondary metabolites, such as antitumor, antibiotics, growth hormone, pigments, and chelated compounds. As mentioned, communication between plant and microorganism occurs through molecular interactions through the exudates of plants' roots and volatile compounds (Ullah et al. 2020).

Their study (Contreras-Cornejo et al. 2019) reported *Trichoderma* fungus's findings when interacting with plants, roots, and seeds. Today, this fungus has multiple applications thanks to its ability to produce secondary metabolites of great interest for medicine, biotechnology, and especially for agriculture, which is the area of interest for this chapter.

Trichoderma fungus regulates plants' growth and development by producing siderophore compounds capable of solubilizing soil nutrients, while the production of antibiotics as a defense against pathogenic microorganisms that attack plants can produce elicitors and VOCs. Their research (Jain et al. 2020) confirmed that it is possible to combat rice diseases caused by the pathogen *Xanthomonas oryzae pv. oryzae* by interacting the rhizosphere of rice with a microbial consortium of two beneficial microorganisms, such as *B. amyloliguefaciens* and *A. spinulosporus.* This showed better results than combating the disease by applying the beneficial microorganisms separately.

Beneficial microorganisms–diseased plant interactions showed differences in the activities of many enzymes, such as superoxide dismutase (SOD), phenylalanine ammonia-lyase (PAL) and peroxide (POD), polyphenol oxidase (PPO) in the rice plant, and higher chlorophyll content was observed, causing higher dry biomass of the plant. Also, 48 out of 55 protein spots analyzed were recognized with direct roles in supporting biotic stress. This study shows that a consortium of two beneficial microbes in the rhizosphere can fight pathogen infections stronger and faster than if treated separately.

Another relevant study is the one carried out by (Gorai et al. 2021), in which one of the species of pathogenic fungus that causes early blight in potato *Alternaria* *alternata*, was isolated to test a bacterial strain and *Bacillus velezensis* that is considered a plant endophyte organism as a biological control agent. The results showed inhibition of 82.34 ± 4.86% of the *Alternaria alternata* fungus, capable of secreting thermostable antifungal metabolites and enzymes that degrade the fungus wall, such as chitinase and β-glucanase, in addition to the production of VOCs.

2.1 Allelochemicals as a Defense of Crops

In agriculture, the allelopathy is known as the bilateral interaction among plants in which a donor plant affects the growth, survival, development, and reproduction of receptor plant by producing secondary metabolites, which are known as allelochemicals (Latif et al. 2017; Schandry and Becker 2019). Recent research on this topic suggests that donor plants secrete allelochemicals through root exudates, aerial plant parts, or even residues in soils (Sodaeizadeh et al. 2010; Effah et al. 2019; Das et al. 2021). The acquired knowledge in biosynthetic pathways derived from that research provides valuable information to maintain agriculture's future on the right path by proposing more sustainable, cleaner, and more efficient practices. Some applications include the usage of bio-based pesticides, better weed management in agricultural systems, crop genetic improvements, and the inclusion of new plant metabolites (Latif et al. 2017).

One of the most relevant studies is that of Sodaeizadeh et al. (2010), in which leaves, stems, and roots of *P. harmala* were used as an herbicide, which showed that the leaves have a higher concentration of phenolic compounds. The data confirmed that a specific concentration of 8 and 12 g/kg of the P. harmala inhibits *Avena fatua* L seedlings' growth by affecting their length, leaf area, and chlorophylls A contents. It is known that the plants' communication can be mediated by volatile organic compounds (VOCs) that include flavonoids, enzymes, and organic acids.

These VOCs can be secreted by plants either above or below ground. A comprehensive literature review by Effah et al. (2019) analyzed how the plants can identify plants of the same family, other families, or events that interact with other trophic levels because of VOCs. In the review by Das et al. (2021), different allelochemicals applied to weed management were examined. The studies showed that these allelochemicals regulated not only plant growth but also cell division and seed germination. It was also identified that allelochemicals were affected by environmental conditions, including phenolic acids, mumylactone, benzoic acid, cinnamic acid, and hydroxamic acids sorgoleone, ethanolamine, hydraxycarboxyamide, ferulic acid, isothiocyanates, and artemisinin. It is essential to point out that the author analyzed the enormous potential of allelochemicals as herbicides and addressed their limitations, stating concrete future research directions. These limitations include the complicated and expensive methods to synthesize and the toxic grade of some compounds like sorgoleone that can produce dermatitis, likewise, ALA toxin, and fumonisins, which are considered as carcinogenic.

Some experiments suggest that the composition of the root exudates changes based on the environment, for example, the soil. The study of Dmitrović et al. (2015) concludes that the seeds of *Arabidopsis thaliana* and *Triticum aestivum* are sensitive to different allelochemicals derived from root exudates from *C. murale*. This was concluded due to the carried-out experiment in which wild-type roots of *C. murale* inhibited the growth of *Triticum aestivum*. Another critical finding obtained from this study is the induction of enzymatic activity, antioxidants, catalases, peroxidases, superoxide dismutase, and gene expression change.

Another study with *M. sacchariflorus* found 22 phenolic compounds in leaf extracts that partially suppressed seed germination and affected the root length of the weed seedlings. Also, it was shown that the result of using a higher concentration of *M. sacchariflorus* extract was lower fresh weight and dry weight of weed, in addition to stimulating the activity of antioxidant enzymes and modifying the chlorophyll and carotenoid content in weeds (Ghimire et al. 2020).

As we can see in the previous studies, the allelochemicals can be present in multiple plant organs, either in the leaves, in the stems, and in the roots, and this shows how they act, directly inhibiting the content of chlorophylls and carotenoids, and stimulate the concentration of antioxidant enzymes. Research in this area is mainly focused on using allelochemicals as bioherbicides to reduce dependence on synthetic herbicides. Alternatively, studies like Sun et al. (2020) used carbon-based nanomaterials to regulate development and growth capabilities by increasing secondary metabolites levels. These strategies could be beneficial to crops by increasing allelochemicals presence. Moreover, in Tables 1 and 2, some positive and negative aspects of applying these new technologies in biological control are shown.

2.2 Interactions Between Plants and Arthropod Herbivores

The interaction between herbivore insects and the plant can derive valuable knowledge to get more sustainable agriculture, even though several positive advantages were reported in the literature, such as producing resistant genes in crops as effector proteins (Jonckheere et al. 2016) and pollination. Some disadvantages have been identified, such as the influence of some herbivores by inducing pests in plants and crops and the disease transmission by injecting viruses into plant tissues during insect–plant feeding interactions.

Recent studies show that communication between herbivorous insects and plants occurs through the salivary glands of insects, which are complex mixtures of proteins capable of interacting with plant cells after secretion, and their composition can be shaped (Weiwei et al. 2018; Chen and Mao 2020). The salivary proteomes of insects give us information on what types of food insects are capable of degrading. Even the salivary proteins that herbivorous insects have can be regulated in response to different diets that give insects the ability to feed on different hosts; these interactions can be helpful in pest management.

Table 1 Applications of the interactions of crops with their environment

Donor specie	Receptor specie	Kind of secretion (exudate, VOCs, salival, etc.)	Molecules of interest	Effect or possible application	Reference
Plant–plant interaction					
P. harmala	*Avena fatua L.*	It was used as a residue of leaves incorporated into the soil	Phenolic compounds	Herbicide	Sodaeizadeh et al. (2010)
Chenopodium murale	*Arabidopsis thaliana* and *Triticum aestivum*	Exudate from the wild root and cultivated root	Not analyzed, only Arabidopsis *thaliana* and *Triticum aestivum* response was measured	Biological weed control	Dmitrović et al. (2015)
Plant–microorganism interaction					
B. amyloliguefaciens + *A. spinulosporus*	Rice plant infected by *Xanthomonas oryzae pv,. oryzae*	Not mentioned, but an antibiotic effect was observed	Possibly antibiotics	Biological control of pathogens	Jain et al. (2020)
Plant–insect herbivores					
Nilaparvata lugens	Rice plant *and N. benthamiana*	Saliva	Effector proteins	Cell death, chlorosis, the dwarf phenotype was caused by salivary proteins presence	Weiwei et al. (2018)

Table 2 General positive and negative aspects in the use of secondary metabolites from the interactions between different organisms

Potential application	Positive aspect	Negative aspect	Reference
Plant–plant interaction			
Herbicide	Weed management	Some allelochemicals are expensive to synthesize	Das et al. (2021)
	Some allelochemicals barely leave little residual toxicity in crops	Some allelochemicals are toxic and carcinogenic to humans	
	Environmental conditions influence the production, release, and phytotoxic levels of allelochemicals		
Plant–microorganisms interaction			
Biocontrol	Provide defense against pathogens	Cause diseases in crops	Jain et al. (2020)
	Promote growth and mitigate biotic stress	–	
	Modulate interaction to benefit plant–microorganism	–	
	–	Some microorganisms of interest to biocontrol are non-cultivable species	Mendes et al. (2014)
Plant–anthropode herbivores interaction			
Pest control	Augmented resistance through the generation of protein effectors	Insects eat crops	Jonckheere et al. (2016)

Other studies such as that of van Bel and Will (2016) and Huang et al. (2020) show that the salivary composition of insects *T. urticae* and *T. tabaci* contains bioactive components which are capable of modifying the defenses of the host plant since the plants perceive the feeding signals of the insects by recognizing the specific salivary components. However, many of these salivary compounds have not been studied yet. Some organic compounds from several plant species have pesticide properties. Studies like (de Oliveira et al. 2019) mixed botanical compounds encapsulated in zein nanoparticles improving their stability efficiency, combining nanoformulations and botanical compounds with pesticide properties, could help create more effective pest management products. As seen from the previous reports, many beneficial effects can be obtained by the complex and not yet fully understood the interaction of plant and many other organisms. Figure 2 compiles the main applications obtained by the interaction between insects, plants, and microorganisms.

Previous studies have analyzed some problems to obtain a representative sample of a native root exudate. One of them is the difficulty of avoiding microorganisms in the rhizosphere that degrade the exudates. The microorganisms can make exudates change their composition, and these exudates can change if the plants have been cultivated in different substrates (van Dam and Bouwmeester 2016). Nevertheless,

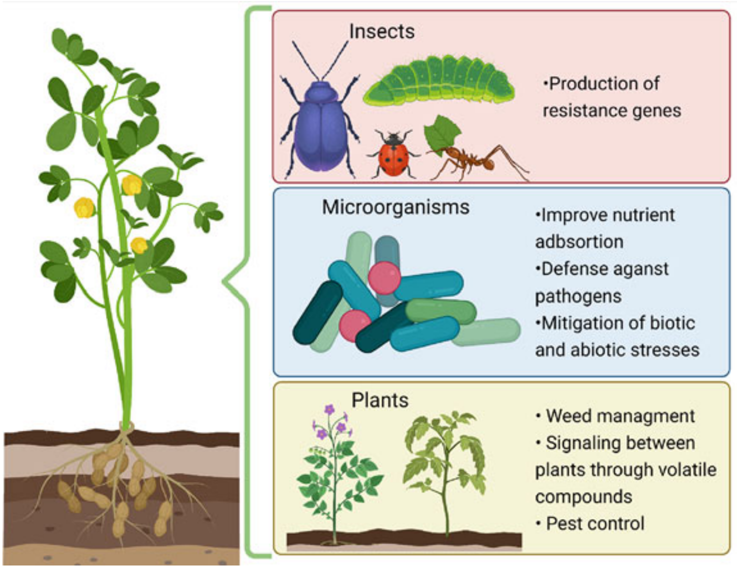

Fig. 2 Applications of plant–insect, plant–bacteria, and plant–plant interactions (created by Biorender.com)

more and more efforts are added to analytical techniques to examine the metabolites or protein implicated as the techniques used in these kinds of studies to analyze the metabolites involved (Hooshmand and Fomsgaard 2021). The analytical techniques may take a lot of time and resources in the experimentation. However, recent investigations like Jonckheere et al. (2016) examine the salivary proteins composition of arthropods for which saliva or salivary glands cannot be isolated easily. Another limitation is that microbiota contains different non-cultivable species. Some techniques help to know more about the species, such as genetic studies (Mendes et al. 2014).

2.3 *Technological Limitations*

According to Drexler (1986), nanotechnology comes from manipulating matter on an atomic, molecular, and supramolecular scale referred to as the particular technological goal of precisely manipulating atoms and molecules to fabricate macroscale products. Aithal and Aithal (2016) developed a concept about ideal technology using nanotechnology by creating a model and identified its essential characteristics categorized as input, output, system, and environmental conditions (Fig. 3).

Input condition characteristic helps to control the fundamental nature of matter for providing solutions for several problems. The improvement and creation of new nanomaterials with many applications and nanotechnology's vision to be applied in

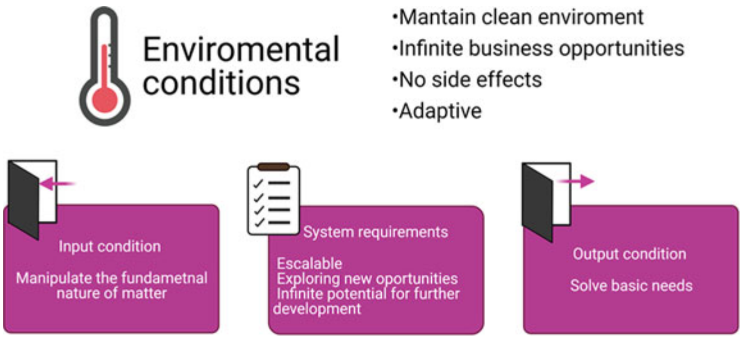

Fig. 3 Ideal technology model using nanotechnology applied to agriculture (created by Biorender.com)

the agricultural sector provide several solutions in developing nanosensors, nanopesticides, and nanofertilizers. Even more, advanced nanotechnology solution could be proposed, as plant gene therapy, creating pest resistant, high yield crops that require less water (Aithal and Aithal 2016).

For output, condition developments should solve basic needs like food, drinking water, renewable energy, etc. In this sense, agriculture uses nanomaterials in order to solve problems in crops that threaten food security every day, for example, to avoid the use of pesticides, uses of new fertilizers, plant disease treatments, and make efficient the consumption of water in crops, as well as electrical energy in the supply chain.

For system requirements, scalability needed for fabrication can be increased, exploring new opportunities and researching new applications will help resolve today's and upcoming problems. Protecting the environment needs to be fundamental nowadays in the design, production, and application of new technologies as well as the protection of human resource less involved in the production, advanced production must be zero or no side effect for being safe even to the environment and living being that could be exposed (Aithal and Aithal 2016).

The intentions of using nanomaterials applied to agriculture have been of significant advance to provide solutions to superior technology objectives. However, technological limitations have been observed in their developments, such as many controversies using nanomaterials in agricultural soils that affect and benefit the microbiota; other examples are mentioned below:

1. Effects of carbon nanomaterials on soil health and global nutrient cycles have been seen (Wu et al. 2020).
2. Different carbon nanomaterials can cause environmental toxicity to crops and rhizosphere bacteria and cause aquatic and terrestrial contamination (Wu et al. 2020; Hao et al. 2019).
3. Some possible impacts of nanoparticles on society about biotechnological approach could be too invasive (Dolez 2015).

4. Nanoparticle toxicity cannot be related to bulk material toxicity due to physicochemical properties. Also, the introduction of nanomaterials to the environment can be due to natural sources or anthropogenic productions, making it difficult to assess the environmental and health impacts of nanomaterials (Kumar et al. 2019).

3 Nanomaterials (Metallic, Oxides, Fibers, and Carbon-Based, Release Route to Plants and Soil)

The increase in the use of nanomaterials causes their presence in the environment to increase, which means an environmental problem that can affect abiotic factors, such as soil, air, and water (Khan et al. 2019).

Toxic behavior and NP translocation have become an attractive research area for understating NP behavior during their interaction with several plant species, aspects like nanoparticle uptake and translocation are not fully understood yet, and it is known that the toxic behavior and interactions will depend on NP physicochemical characteristics as well as the exposure pathways like irrigation, hydroponics as well as interactions between bacteria present in the media and nanoparticles (Pacheco and Buzea 2018).

Different authors have proposed how the different NMs are used in plants depending on the application type to understand the interaction if the NMs come into soils or by foliar application. If the NMs come into through the leaves (foliar), the primary barrier is the cuticle (Raliya et al. 2016). Roots can also permit NMs to be taken from the soil and translocated to other organs in plants due to their pore size of around 5–20 nm (Pacheco and Buzea 2018).

Nanoparticles translocation is highly involved with the cell endodermis structure, where two types can be accounted, passage cell, which has thin walls, and endodermal cells with hydrophobic behavior and thick walls. The passage cells serve as a passage from xylem root hair for water and dissolved solutes. Among the plant tissues that accumulate most NPs during exposure, the xylem serves as a path for distribution to other organs and translocation of NPs (Rajput et al. 2018a), but once the NMs penetrate the plant are two ways for them to move through tissues: the apoplast and the symplast (Pérez-de-Luque 2017).

Cellular transport of NMs can be divide into two ways, apoplast (through the wall) adhering to the root surfaces (Rizwan et al. 2017) and symplast (cell to the cell, mediated by plasmodesmata), particles of sizes of approximately 200 nm tend to travel via the apoplast pathway, while nanoparticles with size less than 50 nm travel through the symplast. The cellular transport limitation suggests that the apoplast pathway is dominant for drop cast methods (Raliya et al. 2016).

During NP penetration, these materials can undergo multiple biological transformations due to multiple molecules that can interact with NPs. These changes involve modifying the toxicity altering multiple stress mechanisms that NPs create during exposure (Rajput et al. 2020).

4 Nanomaterial Interactions with Plants (Toxicity and Benefits)

Plants possess defense mechanisms that protect them against multiple stresses. The defense mechanisms are continuity confronted by synthetic nanomaterial, which has multiple reactions that affect plant biology, even though some nanoparticle–plant interactions are ancient new NPs exposure to plant are a major environmental problem (Dev et al. 2018).

Not only nanoparticle plant interaction must be taken into account, evidence shows that NPs can adhere to plant roots and induce several toxicity mechanisms, but they are also capable of affecting microorganisms present in soil and become a potential risk when they escalate the food chain (Ruttkay-Nedecky et al. 2017).

The interaction between plants and NMs has several properties by which an nanomaterial can become toxic and alter biological systems; in summary, they are:

1. Reactivity or charge: functional groups and chemical characteristics become essential for defining the functionality and bioavailability of NMs (Jeevanandam et al. 2018).
2. Morphology: particle shape defines membrane interaction during endocytosis or phagocytosis processes. Different types of NPs morphology differ from toxicity, although the chemical composition is the same (Turan et al. 2019).
3. Size: smaller particles tend to agglomerate at a lower rate and have higher reactivity (Lead et al. 2018).
4. Particle composition and crystalline structure: several compounds can have multiple crystal structures, and each one toxicity can differ from others (Turan et al. 2019).

Some benefits of NMs are enhancing plant growth and development and the protection process against various abiotic stresses. Also, NMs can antioxidant activities and scavenge reactive oxygen species (ROS). The small size and large surface area of NMs, for example, provide access to toxic metals for binding and thus reduced availability and toxicity (Khan et al. 2019). Figure 4 shows the possible effects on plants when interacting with materials of different physical and chemical characteristics.

Today, the main focus in nanomaterial applications toward plant is the enhancement of secondary metabolites concentration in plants, initially, secondary metabolites are compounds that are synthesized by the plant during exposure to a type of stress which can be caused by other organisms (biotic stress) or environmental conditions such as salinity, temperature, and heavy metals (abiotic stress) (Thakur et al. 2019), in order to mitigate the adverse effects caused by the stress, plants tend

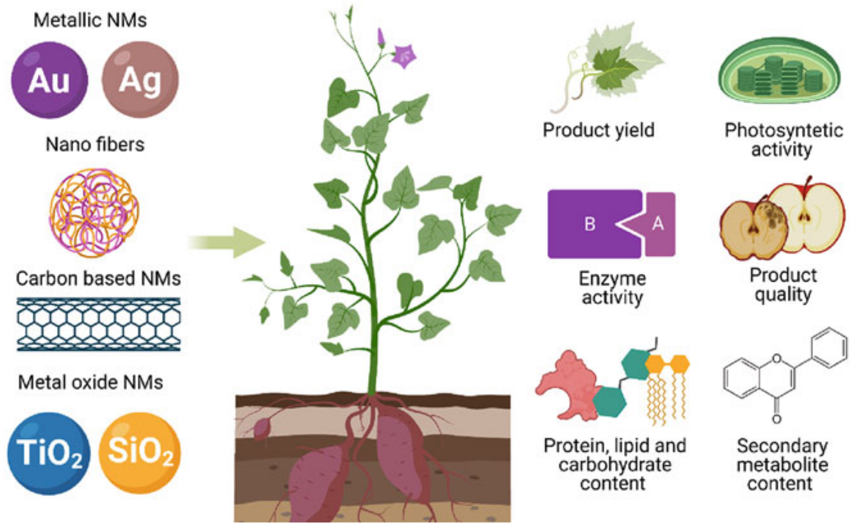

Fig. 4 Effects caused by plant–NM interactions (created by Biorender.com)

to synthesize compounds (secondary metabolites) which have unique properties for protection, increasing survival rate of plants, today, these compounds are being investigate, since their properties and uses are beneficial to human being, these compounds have high nutritional value and antioxidant properties, they also fin applications as colorants, pigments, pharmaceuticals, among others, it is known that nanomaterials can induce the production of these compounds adding the possibility of creating plants with higher value at low costs (Yadav et al. 2012; Zhong 2019).

Li et al. (2020) investigated the effect upon the exposure of NPs on rice, and they founded that. The lack of oxygen functional groups in NPs upregulated the amino acid metabolism, indicating adaptation to abiotic stress. This kind of study helps to understand and predict the design of environmentally friendly nanoparticles.

In summary, no overall conclusion can be drawn about a specific nanomaterial's toxicity for all plant species (Liné et al. 2021). The latest trends in agriculture focus on the use of green nanotechnologies, which exploit biological routes of organisms to synthesize nanomaterials that help to solve fertilization problems, pests, and crop intensification, and the influence of the chemical composition, size, and geometry against the interaction with the crop's environment. Table 3 shows some recent studies with advantages and disadvantages about using nanomaterials that interact with plants, soils, microorganisms, and insects in agriculture.

Table 3 Studies of nanomaterials applied in agriculture based on their composition, size, and shape

NMs (name/size/geometry)	Specific interactions (adhesion–absorption, plant tissue)	Species	Stimuli	Potential application	Advantages	Disadvantages	Ref
Microorganisms							
Fullerene (C60)/around 50 nm/spherical shape	The soil was pre-incubated with *E. coli*	*Escherichia coli*	Activities of extracellular enzymes responsible for degradation of cellulose and hemicellulose in soils treated by C60 and M50	Different applications in agriculture		Profound effects of carbon nanomaterials on soil healthand global nutrient cycles	Wu et al. (2020)
Graphene-based nanomaterials (rGO/Fe_3O_4)/22–35 nm/sheets	Mycelium suspension mixed in fermentation medium with nanomaterial	Medicinal fungi: *Ganoderma lucidum*	Concentration	Elicitation of several metabolites	Production of ganoderic acid		Darzian Rostami et al. (2020)
M50/40 ± 0.83 nm/carbon nanotubes	the soil was pre-incubated with *E. coli*	*Escherichia coli*	Activities of extracellular enzymes responsible for degradation of cellulose and hemicellulose in soils treated by C60 and M50	Different applications in agriculture		M50 possess stronger cytotoxicity to bacteria than C60, CO_2 fixationmicrobial degradation carbohydrates, metabolites, lipids and proteins were affected	Wu et al. (2020)

Insects							
Nanoparticle formulations containing geraniol, eugenol, and cinnamaldehyde	Diffusion-based process	Two agricultural pests: *Tetranychus urticae* and larvae andpupae of Chrysodeixis	Temperature	Pest management	Artificial diets treated with emulsified and encapsulated botanicals showed effects on the mortality and mass of larvae and pupae of *Chrysodeixis*		de Oliveira et al. (2019)
Soil							
Cellulose nanogel/diameter of 116 ± 42 nm/uniform microspheres	Soil	The experiment was in vitro	Capture and stabilization of heavy metal ions	Soil remediation	No hazard due to biodegradable characteristics of cellulose		Hou et al. (2019)
Humic acid-activated dolomite/around 10 μm/not mentioned	Sandy soils	NA	Change of soil characteristics	Remediation of metal-polluted soils	Immobilizing toxic elements in the sandy soils		Liu et al. (2021)
MSN−TA/about 423 nm/spherical morphology	Electrostatic interaction with soil	*Cucumis sativus L.* was used to show that the treatment did not affect the plant	pH, ionic strength, and temperature-responsive	Charge-carrying agrochemicals	MSN−TA can decrease the soil leaching of 2,4-D sodium salt		Cao et al. (2018a)
Plants							
Fe–EDDHSA–$CaCO_3$/<10 μm	Absorption mostly in leaves	*Actinidia deliciosa A*	Alkaline and pH conditions				Baldi et al. (2018)

(continued)

Table 3 (continued)

NMs (name/size/geometry)	Specific interactions (adhesion–absorption, plant tissue)	Species	Stimuli	Potential application	Advantages	Disadvantages	Ref
				Strategy for reducing Fe-chlorosis	Iron chlorosis treatment in kiwi fruit plants		
Methacrylate lignin sulfonates/200−300 nm/spherical nanoparticles with a core−shell morphology	NA	NA	NA	Lignin sulfonate nanocarriers as agrochemical	Two commercial fungicides were encapsulated (pyraclostrobin and prothioconazole) into the lignin sulfonate nanocarriers, which are currently used in spraying applications for wheat, almonds, peanuts, oats, and so forth		Beckers et al. (2020)
Thiamine loaded chitosan nanoparticle/10–60 nm/amorphous structure	Leaves and roots	Chickpea	Induction of defense enzymes in leaves and roots	NPs can be used as a stimulator and defense activator	NPs enhanced seed germination and growth of chickpea seedlings		Muthukrishnan et al. (2019)
		Corn leaves	pH and concentration	Ferrous foliar fertilizer	Ferrous foliar fertilizer		Wang et al. (2016)

CFFF/around 10 μm/ microfibers	Adhesion of foliar fertilizers on the corn leaf surface				promotes the growth of crops		
LC@PNIPAm–GO/about a few hundred nanometers	Adsorption in roots and shoot	Corn seedlings	Different temperature	Nanocomposite carriers of pesticide	Potential for improving pesticide efficacy		Wang et al. (2021)
PRO-MON-CaC/ around 65 nm/regularly spherical	Foliar adherence	*S. sclerotiorum* on rapeseed plants (*Brassica napus L.*)	pH and reduction dual-stimuli-responsive release performances	Biomaterial for biodegradable and smart pesticide delivery	NMs showed fungicidal activity against *S. sclerotiorum*		Gao et al. (2020)
Cu + PSI NPs/~14.2 nm	Absorption in seedling root andshoot	*Zea mays L.*	Concentration	Enhancement of seed germination and reduction of metal toxicity	NPs can be us for enhancing germination and protection against heavy metals		Xin et al. (2020)
Fullerene (C60), reduced graphene oxide (rGO), and multi-walled carbon nanotubes (MWCNTs)	Shoot and roots	Rice	Increased SOD and POD activity	The use of a variety of carbon nanomaterials are already applied but have adverse environmental effects that need to be studied		Carbon NMs caused toxicity to rice and bacterial community	Hao et al. (2019)
Single-walled carbon nanohorn (SWCNH)/pipe diameter, 2–5	Arabidopsis seedlings and root	*Arabidopsis*	Increased amino acid, sugar, and organic acid levels	Growth promoter	Regulation of plant growth and secondary		Sun et al. (2020)

(continued)

Table 3 (continued)

NMs (name/size/geometry)	Specific interactions (adhesion–absorption, plant tissue)	Species	Stimuli	Potential application	Advantages	Disadvantages	Ref
nm; pipe length, 10–20 nm/nanohorns					metabolite content increase		
Aba@HMS@P (GMA-AA)/190 nm/spherical nanoparticles	Adhesion properties on rice leaves	*C. medinalis* used as a model for bioactivity	Nanomaterial stable at pH values of 5 and 7 after a prolonged incubation time	Pest management	*Medinalis larvae* could control the pests for more than 21 days on sustained release		Gao et al. (2019)
PHMCN-Se/~100 nm/spherical shape	Absorption mostly in leaves	Leaves of vegetable	Different pH conditions, phosphate, and carbonate solutions with different concentrations	Se-enriched fertilizer	Selenium as trace element could help to promote the growth and development of plant		Zhang et al. (2018)
GA3-HMSN/Fe_3O_4/50 nm/nanovalvules	MS medium withnanomaterials	Cabbage and *A. thaliana*	Triple-stimuli: pH, competitive, and ultrasound	Nanocarrier for plant genes, fertilizers, and pesticides for growth promotion, NPs magnetic characteristic can be used for remote control by magnetic fields	Promote plant growth		Li et al. (2019)

4.1 Metallic Nanomaterials

Metal exhibits different physicochemical properties, such as excellent optical, electrical, catalytic, and magnetic behavior, chemical and mechanical stability, ease of surface modification, and a large surface area for reactions (Singla et al. 2016). The impact of nanoparticles upon them is not well-studied. Metals like silver (Ag), copper (Cu), aluminum (Al), nickel (Ni), and iron (Fe) are most commonly used in industries and, therefore, are mainly studied for their impacts on different plants (Rastogi et al. 2017).

Different plants exhibit specific behaviors toward the presence and excess of metal ions that can be released from metallic NPs. Some plants can be tolerant toward metals, limiting their uptake and restricting the NP transport through the plant tissues, only allowing them to be stored in the root (Rajput et al. 2018b).

As mentioned before, nanomaterials can induce secondary metabolite production, as shown in *Caralluma tuberculata* callus cultures exposed to Ag NPs. The interaction of the callus with the NPs leads to an increase in the phenolic compound, flavonoid, and a higher antioxidant activity and antioxidant enzymes like superoxide dismutase, peroxidase, and ascorbate peroxidase. As mentioned by the authors, these results can be further applied in the mayor scale for producing high-interest compounds (Ali et al. 2019). An enhancement of secondary metabolites content was also achieved in *Prunella vulgaris L.* callus exposed to silver. Gold NPs in different ratios, the different rations, and the combinations of naphthalene acetic acid achieved different beneficial effects like increased protein content, enhanced callus proliferation, higher biomass, and an increase of phenolic, flavonoid, and antioxidant enzymes concentrations (Fazal et al. 2016). A positive effect with the use of Cu and Au NPs was also observed in root cultures of *Stevia rebaudiana* (Bert.), where the presence of several ratios of NPs in the medium increased biomass accumulation and phenolics and flavonoids production (Ghazal et al. 2018).

The increase of secondary metabolites and antioxidant compounds in plants during NP interactions is mainly caused by ROS production, which generates a stress factor in the crops. ROS production is the primary key to induce interest compound production, although these reactive species' overproduction can lead to profound cellular damage in plant tissue affecting its development (Shabbir et al. 2019).

4.2 Oxide NMs

Another advantage of NP application for crops is preventing biotic or abiotic stresses, such as heavy metal stress. Some metal oxide NPs have demonstrated the ability to reduce the bioaccumulation of heavy metals, such as lead, as demonstrated by the exposure of TiO_2 to rice in the presence of lead. However, care must be taken with nanomaterials since they are translocated into plant tissues leading to a food safety issue (Cai et al. 2017). ZnO nanomaterials showed a high dissolution rate accompanied by a high binding activity causing accumulation in the root tissue of *Vigna angularis*, leading to a reduction of physiological activity. TiO_2 nanomaterials applied to the same type of crop showed opposite effects improving plant physiology. However, both materials are photocatalytic and have the ability to generate reactive oxygen species (ROS). Only the ZnO nanomaterials generated oxidative stress-reducing chlorophyll content as well as carotenoids (Jahan et al. 2018). Similar results where ZnO NPs showed higher toxicity compared to TiO_2 when applied to *Hordeoum vulgare* L. (Doğaroğlu and Köleli 2017).

Although some experimentations with photocatalytic NPs show affectation toward plants, these NPs can also be used to enhance some aspects of plant development such as growth rates or the production of secondary metabolites as shown with TiO_2 applied to *Vetiveria zizanioides* L., where the chlorophyll and the essential content were augmented (Shabbir et al. 2019). *Nigella arvensis* exposed to TiO_2, Al_2O_3, and NiO showed an increase in quercetin content after exposure of 1000 and 2500 mg/L (Modarresi et al. 2020).

Iron oxide nanoparticles are also being investigated in order to find interesting applications toward there is in agriculture. Many effects caused by these types of nanoparticles had been found, such as a higher resistance toward salinity stress. Apart from mitigating the effect caused by the abiotic stress, NPs cause a higher content in several proteins and rosmarinic acid (Modarresi et al. 2020). The use of nanoparticles can modulate plant defense mechanisms toward pathogenic microorganisms. These can also be achieved for increasing plant protection to viruses as observed with tobacco plant treated with iron oxide NPs through foliar exposure, Fe_3O_4 causes reactive oxygen species production augmenting antioxidant enzymes activity, and NPs also upregulated salicylic acid gene expression which helps with the protection against tobacco mosaic virus (Cai et al. 2020).

The release of metal ions must be taken into account, since they are involved in the toxicity effect expressed in the plant when interacting with crops. The release of those kinds of ions can be an advantage for helping crops that have a lack of micronutrients such as iron or zinc, although the release of ions can also cause adverse effects in plant development, such as altered root morphology in wheat exposed to CuO nanoparticles (Adams et al. 2017).

4.3 Organic NPs and Fibers

Nanofibers can also find promising application in agriculture helping with the prevention of plant diseases as well as secondary metabolite modulation and mitigation of biotic and abiotic stresses, chitin nanofibers which is the main component of arthropod exoskeletons show interesting properties when the fiber is brought to the nanoscale, *Arabidopsis thaliana* induced ROS induction and the generation of genes related to defense in crops, the interaction of chitin nanofibers reduced bacterial and fungus infection in *Arabidopsis thaliana* demonstrating a promising activity toward the enhancement of defense responses of plants (Egusa et al. 2015), chitin nanofiber stability to enhance plant defense mechanisms was also demonstrated when fibers were exposed to *Vigna radiata* and *Capsicum annuum*, the presence of chitin elevated the chitin-related genes and the salicylic acid content, these effect helped to reduce the fungal spread in both species of plants (Um e et al. 2021), not only plant mechanism can also be enhanced by the presence of nanofibers, chitin has also the ability to improve the nutrient uptake like nitrogen and carbon as shown in tomato plants (Egusa et al. 2020).

Organic nanoparticles such as chitosan can also be coupled to metals to increase beneficial traits when interacting with plants. Maize treated with Cu–chitosan NPs increases the defense mechanism of maize toward curvularia leaf spot disease. These NPs also enhance growth, increasing height, root length, and enchasing chlorophyll content. Adding Cu to the NPs helps growth and disease control by releasing copper into the media (Choudhary et al. 2017). Nanomaterials can be applied in different stages such as floriation or germination in order to improve the development. Chitosan nanoparticles can also serve as growth promoters for increasing the growth rates of seeds, such as rice (Divya et al. 2019).

4.4 Carbon-Based NMs

This category is held by multiple carbon structures like carbon dots, nanotube, nanohorns, nanofibers, and more. One interesting fact about carbon nanotubes is that these structures can penetrate the seed coat and support the water uptake. In the plant, multiwalled carbon nanotubes (MWCNTs) can translocate from roots to the stem and helps the water and nutrient uptake, augmenting the transport efficiency and enchasing plant growth (Mohamed et al. 2018).

MWCNTs applied in the culture medium of *Catharanthus roseus* showed a more significant increase in many growth parameters, such as leaf width, leaf area, fresh weight, total biomass, and root length.

Nanotubes' presence also increased chlorophyll, carotenoids, phenols, alkaloids content, and antioxidant enzyme activities (Ghasempour et al. 2019). The exposure time of different nanomaterials is essential to assess the possible risk caused by nanomaterials in the ambient and the possible long-term toxicity toward the crop. The effect observed will depend on nanoparticle characteristics, plant species, and exposure time. As shown by Lahiani et al. (2018), 20-week long-term exposure to MWCNTs to barley, soybean, and corn showed no longer term toxic effect. However, the carbon nanomaterials had the ability to translocate into several organs, adding another aspect of risk assessment. Carbon nanotubes can also protect crops against organic contaminants such as paraquat through surface sorption (Fan et al. 2018).

Not all the effect observed with nanomaterials' exposure has a positive effect in plant development, carbon nanomaterials have shown promising features for advanced techniques for agriculture managements. However, some plant species can be sensible toward the exposure of several nanomaterials such as *Cucurbita pepo L.*, which was submitted to toxic effect after the exposure of MWCNTs in several concentrations (125–1000 μg mL^{-1}). The exposure caused a lower germination and growth rate, and the negative effect was attributed to the injury caused by tissue damage caused by hydrogen peroxide, electrolyte leakage, and malondialdehyde content (Hatami 2017). Some other benefits, as well as detrimental effects caused by nanomaterials, are shown in Table 4.

5 Nanomaterial Interaction with Microbes (Toxicity and Benefits)

It is known that nanomaterials are physicochemical characteristics which differ from its bulk counterpart, this adds a new complexity level for understanding the mechanism of interactions with several living being, researches in plant demonstrate that nanoparticles can have beneficial and detrimental effects in many species, the effect observed will depend on a set of nanoparticle characteristics as well as the experimental model selected for the nanomaterial exposure, size, surface charge, dose, time exposure, type of nanomaterial, crystal structure form part of the main characteristics that will define the nanoparticle toxicity mechanisms (Dietz and Herth 2011; Cheng et al. 2016; Banerjee and Kole 2016) when interacting with any living being, crops are not the only organisms that are affected when nanomaterials are introduced to the soil, bacteria, fungi as well as other organisms come to interact with those exogenous materials, and as seen with plant nanomaterial–bacteria interaction can lead to benefits as well as adversities (Dimkpa 2014; Bundschuh et al. 2018).

The bactericidal feature of nanoparticles can be applied for fighting pathogenic bacteria that cause diseases to crops, as seen from medical research of nanomaterials, they are considered an alternative to antibiotics by effectively preventing microbial resistance to drugs, investigation of new effective bactericidal materials is essential to combat drug and bactericidal resistance, and NPs have been established as a promising approach to solve this problem (Wang et al. 2017b); nevertheless, care must be taken for not affecting or diminish growth-promoting bacteria that are essential for a healthy and efficient development of crops, focusing on benefits some nanomaterials can lead to an increase of bacteria strains that are beneficial to soil and plant development by modifying metabolite profiles, but nanomaterials that have positive effects toward some organisms will not have the same effects to other leading to a complex problem for nanotechnology applications without compromising multiple organisms with different characteristic that will react differently with nanoparticles (Dimkpa 2014). Figure 5 shows some of the effects observed through the interaction of nanoparticles with soil bacteria.

Table 4 Toxic and beneficial effects of NMs in plants

Nanomaterial	Size	Conditions	Application	Plant/ organism	Results	Ref.
Ag NP	Between 7 and 14 nm	The soil had a pH of 5.5 ± 0.1	10, 25, 50 mg kg^{-1}	Eartwarm (soil)	The 72 weeks long soil incubation study revealed that deterioration in soil depends on the levels and NPs time exposure. Retardation in nutrient availability	Das et al. (2018)
Mesoporous carbon (MCNs)	80 and 150 nm	Hydroponic culture	0, 10, 50, 150 mg L^{-1} for 20 days	*Oryza sativa L.*	Exposure to 150 mg L^{-1} resulted in a decrease in root length and shoot while at 150 mg L^{-1} significantly reduced the root and shot lengths	Hao et al. (2019)
CeO_2 NPs/PVP–CeO_2 NPs	The average size of 19 nm/average size of 10 nm	The seeds were germinated in moist soil five days	Known amount of CeO_2NPs was added to the dry soil) to achieve a concentration of 100 mg kg^{-1}	Glycine max (L.)	NPs exhibited the potential to enhance the growth of soybeans at high soil moisture contents	Cao et al. (2018b)
Cu–Zn/CNFs	34 ± 6 nm	Planter pots were filled with 500 g of soil	–	*Cicer arietinum*	The germinations of the plants grown without control or with a single metal-based nanofertilizer were much smaller than those grown using the nanomaterial	Kumar et al. (2018)
Fe_3O_4 NPs	105 nm	NPs were suspended in deionized water (solution of 1 g L^{-1} for each metal element of NPs)	20 μg mL^{-1} of NPs was added to the soil	Tomato	Promoted the root growth	Vittori Antisari et al. (2015)
CuO NPs	50 nm	Germination of seeds was in glass Petri dishes (10 cm) in	The NPs solution was used at 0–1600 mg/L	*Brassica juncea*	A low concentration of NPs was accumulated in plants	

(continued)

Table 4 (continued)

Nanomaterial	Size	Conditions	Application	Plant/ organism	Results	Ref.
		the dark, at 25 ± 2 °C, and at 50% relative humidity			and showed tolerance against stress	Rao and Shekhawat (2016)
TiO_2	21 nm		0, 50, 100, 150, 200 and 250 mg L^{-1}	*Mentha piperita L.*	NPs enhanced growth, photosynthesis, enzyme activities, and nutrient status	Ahmad et al. (2018)
Mn_2O_3	50 nm		25, 50, 100, and 200 mg L^{-1}	*Atropa belladonna L.*	NPs caused changes in morphology and physiology characteristics like relative water content and total chlorophyll	Tian et al. (2018)

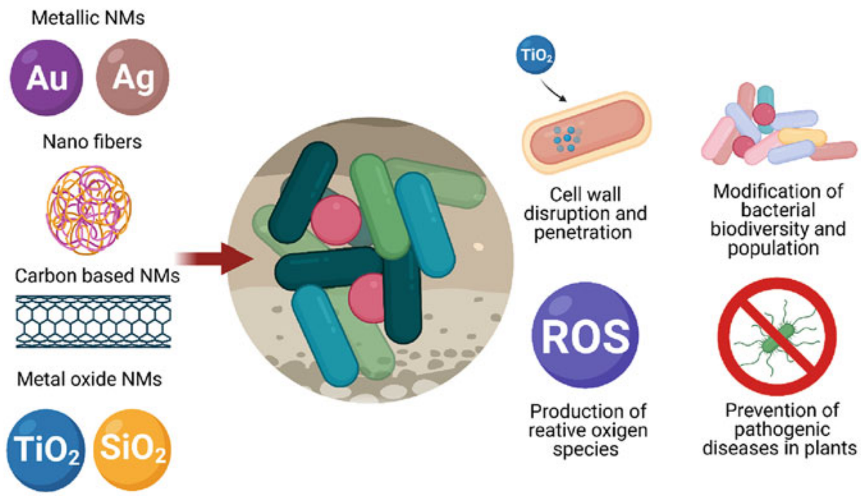

Fig. 5 Effects caused by bacteria–NM interactions (created by Biorender.com)

5.1 Metallic Nanoparticles

For all of the above, it is crucial to consider those different mechanisms involved in the antimicrobial activity of NPs. Other toxicities that NPs can exhibit are dependent on the two significant factors: nature of NPs and interaction with different microbial species (Niazi and Gu 2009).

As shown with metal oxides, metal nanoparticles can also have beneficial and detrimental effects on soil microorganisms, among the most used type of metal to make nanoparticles we find silver and gold, silver nanoparticles have promising antibacterial properties that can be exploited to fight pathogenic bacteria, while gold nanoparticles can act as nanobiofertilizers with the ability to accelerate growth of several growth-promoting bacteria strains like *Pseudomonas fluorescens*, *Pseudomonas elgii*, and *Bacillus subtilis* as shown in Shukla et al. (2015), Au NPs surface can also be modify for augmenting their potential as nutrient delivery agent as showed with Au NPs which were coated with citrate and polyvinylpyrrolidone (PVP), coated NPs (PVP) increased stimulation of soil enzyme activity at low concentrations, the increase effect of soil enzyme was also obtained with NPs of 50 nm after 30 days of exposure, the *Actinobacteria* and *Proteobacteria* present in soil increased after exposure of gold NPs in soil indicating that modification of standard nanoparticles could lead to higher beneficial effects (Asadishad et al. 2017).

For metal NPs, the accumulation of these materials in the cell wall causes leakage of protons and, in some scenarios, the formation of pits in the membrane, leading to disruption of DNA replication and altered respiration. The action of NMs depends on the bacterial cell's components and structure (Raghunath and Perumal 2017).

Table 5 Metal nanoparticles interaction and effects with soil bacteria

NPs	Size	Concentration	Effect	Reference
Ag	20 nm	100 mg kg^{-1}	NPs increased soil pH and altered bacterial community structure, affecting bacteria related to carbon, nitrogen, and phosphorus cycling	Zhang et al. (2020)
Ag	–	0.01–1 mg AgNP kg^{-1} soil	Short term exposure increased *Acidobacteria*, *actinobacteria*, and *Bacteroidetes*, although a long-term exposure (1 year) reduced *Acidobacteria*, *Bacteroidetes*, and *beta-Proteobacteria* population	Grün and Emmerling (2018)
Ag	11.79 ± 4.74 nm	15 μg of NPs g^{-1} (microcosms)	The NPs altered proteobacteria, Actinobacteria, and *Firmicutes phyla*	Chavan and Nadanathangam (2019)
Ag	50 nm	10, 50 and 100 mg kg^{-1}	The population of multiple phyla, such as Acidobacteria, Actinobacteria, Cyanobacteria, and Nitrospirae decreased while Proteobacteria and Planctomycetes increased after silver exposure	Wang et al. (2017a)

Ag nanoparticles which show bactericidal effect could be more challenging to apply to soils, since their bactericidal activity applies more or less to beneficial an harmful bacterial, these nanoparticles applied in soil with the presence of *Bacillus cereus* and *Pseudomonas stutzeri*, showed bactericidal effects at a concentration of 5 mg L^{-1} after 48 h, NPs exposure also showed a decrease in bacterial transcriptional response that was attributed not only to nanoparticles but soil, suggesting that NPs mechanisms are subjected to soil matrix characteristics (Fajardo et al. 2014), as suggested before Ag NPs could be potentially harmful for several organisms including the ions that can release which have been found up to 20–48 times nor toxic toward bacteria involved in the nitrogen cycle (Yang et al. 2013), as mentioned before NPs present in soil and its activity will depend on soil properties including the compounds present in the medium such as humic acids and other ions present in water as investigated by Calder et al. (2012), where Ca^{+2} ions as well as humic acids affected Ag NPs bioactivity, crating agglomerates and NPs coated with organic matter that mitigate the toxicity of NPs present in soil. More studies are presented in Table 5.

5.2 *Metal Oxides*

The oxides of transition metals form the metal oxide; they possess unique electronic properties to treat antibiotic-resistant bacteria (Raghunath and Perumal 2017). Some examples of nanometal oxides are titanium oxide (TiO_2), zinc oxide (ZnO), cupric oxide (CuO), magnetite (Fe_3O_4), and magnesium oxide (MgO). These examples have been reported to have important antimicrobial properties, which depend mainly on their chemical composition, shape, and size (Vidic et al. 2016).

Studies of nanostructured materials reported the significant processes underlying the antibacterial effects of NPs: some of them is the formation of reactive oxygen species (ROS), membrane damage, homeostasis loss due to metal ions, protein and enzyme alterations, genotoxicity, and inhibition of signal transduction (Vidic et al. 2016; Raghunath and Perumal 2017; Wang et al. 2017b; Hemeg 2017). Using these mechanisms, NPs have become an attractive technique for treating microbial cells investigators have worked out on the toxicity of organic and inorganic nanomaterials to microbial cells. Studies revealed that carbon-based materials, oxides, and metal nanoparticles have microbial cytotoxicity. Also, the toxicity of NPs on microbial cells has been analyzed, showing that the generation of ROS leads to membrane damage in microbial cells (Sardoiwala et al. 2017).

The oxidative stress process comprises reactive oxygen species (ROS), reactive molecules with highly oxidating capabilities. The NPs can generate multiple types of reactive oxygen species; these ROS can be involved oxidation or reduction processes causing harmful effects on cells such as DNA damage (Abdal Dayem et al. 2017). Alteration in the mechanisms of production and elimination of ROS, in favor of production, originates oxidative stress in the cell. MgO NPs can generate O^{2-}, while ZnO NPs can generate H_2O_2 and OH but not O^{2-}. On the other hand, CuO NPs can produce several types of reactive oxygen species. ROS molecules differ from different degrees of reactions, causing acute stress to microbial death; when affected by these molecules, plants can neutralize antioxidant production, such as secondary metabolites or antioxidant enzymes (Hemeg 2017).

Studies indicate that MgO NPs can modify expression levels of multiple metabolic proteins, reducing bacteria's cell metabolic activities. CuO NPs can also alter the expression levels of proteins related to nitrogen metabolism, significantly inhibiting nitrate reductase activity (Wang et al. 2017b).

NPs can also alter protein structure by metal ion release with catalyzes protein oxidation, carbonyl groups bound to proteins, and their carbonylation level can be used as for determining oxidative damage caused by the NPs, by altering protein structure in structures such as enzymes, proteins, and starch to degrade or make the inactive, as seen with CuO; NPs caused a significant alteration in protein expression altering several mechanisms related to electron transfer, metabolism, and transport (Hemeg 2017).

The inhibition effect of bacterial growth caused by nanoparticles is thought to be due to several mechanisms, including the generation of ROS. However, the growth-promoting effect on bacterial strains of importance to plant development is not fully understood. Even though nanotitania has shown a detrimental effect on bacteria, nano-TiO_2 can also have the ability to increase bacteria (*Bacillus amyloliquefaciens*) adhesion capabilities to roots, as observed with *Arabidopsis thaliana* (Palmqvist et al. 2015). In Table 6, the multiple effects of several metal oxides on soil bacteria are presented.

Cell wall accumulation of nanomaterials can lead to changes in the permeability activity of cell walls. In some cases, bacterial death can be caused by the release of

Table 6 Metal oxide nanoparticles interaction and effects with soil bacteria

NMs	Size	Concentration	Effects	Reference
SiO_2	15 nm	10 mg L^{-1}	A combination of NPs and PGPB showed enhanced growth and metabolite content in maize	Kukreti et al. (2020)
ZnO	90 ± 10 nm	1–100 mg kg^{-1}	ZnO NPs at 10 mg kg^{-1} altered soil bacteria community structure	Xu et al. (2018)
CuO TiO_2	TiO_2 (20 nm) CuO (40 nm)	100–1000 mg kg^{-1}	TiO_2 NPs slightly affected microbial biomass in paddy soils, while CuO_2 showed higher toxicity toward microbial community and affecting microbes by modifying nutrient bioavailability	Xu et al. (2015)
ZnO	25 nm	0.25- and 0.50-mL L^{-1}	ZnO reduced disease indices for soft rot, bacterial pocket, and leaf spot caused by bacteria	Siddiqui et al. (2019)
TiO_2	21 nm	100 μg mL^{-1}	Reduction of rhizosphere bacterial count, plant root, and stem growth by the presence of NPs in Buttercrunch lettuce seeds	Kibbey and Strevett (2019)
CeO_2	–	0.1–10 mg L^{-1}	Ceria nanoparticles inhibit bacterial growth at 50 mg L^{-1}. Ceria NPs also inhibit B diazoefficcin s nodulation affecting N_2 fixation	Mortimer et al. (2020)
ZnO	–	100 and 500 mg kg^{-1}	NPs altered *Nitrospirae* and *Actinobacteria* soil communities after a 90-day treatment affecting carbon a nitrogen cycling	Chen et al. (2021)
SiO_2	20 nm	50 mg of SiO_2 every 3 days for 15 days	*Rhodobacteraceae* and *Paenibacillus* bacteria, and *Chaetomium* fungi involved in the nitrogen and carbon cycle were increased	Tian et al. (2020)
ZnO CuO Al_2O_3 TiO_2	–	0–1000 μg mL^{-1}	Bacterial strains (*Azotobacter chroococcum*, *Bacillus thuringiensis*, *Pseudomonas mosselii*, and *Sinorhizobium meliloti*) were more affected by ZnO, disrupting surface adhering ability and inhibiting cell respiration	Ahmed et al. (2020)
CuO	15–20 nm	333 and 1000 mg kg^{-1}	Single and repeated applications of nanomaterials show no significant difference in nitrifying bacteria. Ag NPs showed higher toxicity toward microflora compared to CuO	Schlich et al. (2016)
CuO	50 nm	500 mg Cu kg^{-1}	CuO NPs showed a toxic effect on maize and microbes in the treated soil due to copper ions' release	Pu et al. (2019)
ZnO CuO	ZnO (100 ± 25 nm) CuO	10 mg kg^{-1}	Low concentrations of nanoparticles showed higher microorganism growth and activity	Jośko et al. (2019)

(continued)

Table 6 (continued)

NMs	Size	Concentration	Effects	Reference
	(50 ± 10 nm)			
TiO_2	21 nm	1 and 500 mg kg^{-1}	NPs were showed no change in microbial community abundance in several soils except for silty clay, where it reduced the carbon mineralization	Simonin et al. (2015)

molecules and intracellular factors. The effect observed will depend on the cell wall structure composition, which can change among different types of bacteria, thus showing different effects (Raghunath and Perumal 2017).

When metal ions are present in excess in the soil, they can alter and disbalance several mechanisms for microbial survival. Metal ions assist coenzymes, cofactors, and catalysts; when these ions are in excess, metabolic disorders can arise, leading to adverse effects such as DNA structure modification (Vidic et al. 2016).

5.3 *Organic NPs and Fibers*

Research of organic NPs and nanofiber focuses on the immobilization of bacteria in the fiber structure or inside NPs to use them in production processes, bioremediation, or crop production improvement. The encapsulation of bacteria comes with significant advantages, such as more excellent protection against environmental stresses or chemical compounds detrimental to plant growth promoting bacteria. Furthermore, the material in which bacteria are encapsulated slowly delivers the microorganisms into the media, adding a control release factor and higher selectivity and better bioavailability. Most of the encapsulation material supposes no environmental risk, since they are easy to eliminate by natural processes. These eliminate the future risk assessment which inorganic nanomaterials possess (Damasceno et al. 2013; Vejan et al. 2019).

The application of soil bacteria encapsulated with polyvinyl alcohol (PVA) on soybean seeds showed enhanced nodulation in roots compared to seeds inoculated with non-encapsulated bacteria. Furthermore, bacteria encapsulation helps protect rhizobia against stress factors and increases colonization (Damasceno et al. 2013).

Better conservation of bacteria was also achieved using electrospinning technic to encapsulate rhizobacteria. These approaches lead to improved germination, survival rate, root growth, and plant characteristics like leaf number and shoot dry weight without affecting the beneficial traits of rhizobacteria due to the immobilization (de Gregorio et al. 2017). PGPR could be immobilized in several nanofiber types, improving crop development without compromising other microorganisms present in soils. The main advantages offered by bacterial encapsulation with nanofiber or organic NPs are shown in Fig. 6.

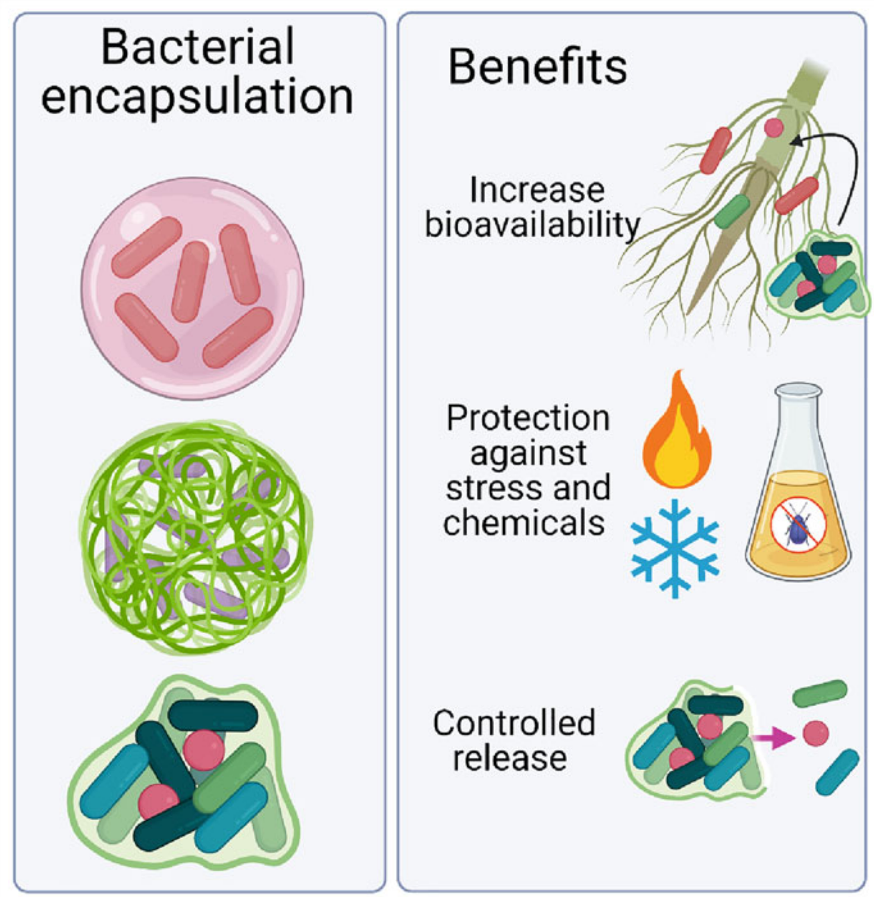

Fig. 6 Main advantages of bacterial encapsulation by nanomaterials

5.4 Carbon-Based Nanomaterials

Carbon-based nanomaterials are also considered excellent materials for agriculture, since some studies realized in plants found beneficial impacts like increased growth. Carbon-based nanomaterials are composed of several structures, where each possesses chemical and structural characteristics that will alter the mechanisms of interactions with soil organisms. As viewed with graphene oxide, it was found that the application in the agricultural field could be detrimental to several bacterial strains like *Bacillus marisflavi*, *Bacillus cereus*, *Bacillus subtilis*, *Bacillus megaterium*, and *Bacillus mycoides* since the nanomaterial decreased cell viability based on its concentrations and exposure time (Gurunathan 2015).

The importance of the microbiota in soils has been mentioned in previous studies showing many advantages in the yields and health of crops. Many controversies

Table 7 Carbon nanomaterials interaction and effects with soil bacteria

NMs	Size	Concentration	Effect	Reference
C_{60}, Multiwalled carbon nanotubes M50, M8	C_{60} M50 (<50 nm) M8 (<8 nm)	300 and 3000 mg/kg	Carbon nanotubes affected bacterial biomass (47.8–60.7%) and fungi communities (31.4–71.6%, being the fungal communities more sensitive to M8 nanotubes	Zhang et al. (2018)
Carbon nanotubes	MW20 (10–20 nm) MW30 (20–30 nm) MW50 (30–50 nm) SW (3.441 ± 0.143)	0.05%, 0.1% and 0.5% mass fraction	Single-walled nanotubes affected soil bacterial community diversity and composition of specific phyla, which recovered after 56 days of exposure	Wu et al. (2020)
Single wall carbon nanotubes	length (1.02 μm) diameter (1.0 nm)	(0.03 to 1 mg g^{-1} soil	SWNTs had a negative relation with bacteria abundance in soil	Jin et al. (2014)
MWCNTs Graphene nanoplatelets Carbon black	–	0.1 or 10 mg L^{-1}	Plant growth inhibition caused by MWCNTS and CB at 50 mg L^{-1}, MWCNTs inhibit nodulation in soybean affecting N_2 fixation	Mortimer et al. (2020)

exists with the use of nanomaterials in agricultural soils that affect and benefit the microbiota. A study executed by (Wu et al. 2019) reveals the effects of carbon nanomaterials on soil health and global nutrient cycles. Also, they had stronger cytotoxicity to bacteria, but on the other hand, another study used medicinal fungi *Ganoderma lucidum* as elicitors to produce valuable metabolites as ganoderic acid (Darzian Rostami et al. 2020).

Cucumber, tomato, rapeseed, and maize showed different effects when exposed to carbon nanotubes, where cucumber and rapeseed showed positive effect related to increase in leaf biomass as well as chlorophyll, maize showed negative impact after exposure, where nanotubes caused a reduction in plant height, on the other hand, tomato showed no changes related to the exposure on nanotubes showing the importance and difference between plan species when interacting with one type of nanomaterial, as said by Liné et al.'s differences in cell wall composition among species could be an essential characteristic in determining toxicity effects of nanomaterials (Liné et al. 2021), as shown in Table 7.

6 Conclusions

As presented in this chapter, nanotechnology can be a valuable tool for agriculture, offering to obtain crops with better development and nutritional characteristics. Nanomaterials that are present in the soil can have a profound impact on the rhizosphere and the organisms that compose it. The effects observed can be positive, like enhanced development of crops or the increase of plant growth-promoting bacteria populations, which helps fix multiple essential micronutrients, eliminating pathogenic organisms that affect plants' development achieved with the use of nanomaterials. However, attention must be taken to reduce the adverse effects on organisms beneficial for crop developments. In this way, great care must be paid to nanomaterials' effects in contact with organisms such as plants and bacteria, seeking to take advantage of their properties and reduce their negative aspect, so beneficial organisms present in soils are not affected by these materials.

Plant and nanomaterial interaction depends on the nanomaterial's properties and the plant's complex physiology and medium. It is complex the understanding interaction of each NMs and each plant. Exist several proposals that help to visualize the internalization of some NMs into some species, according to the general characteristics of plants' physiology, follow two principal routes starting of the way application. The main factor to understand is the medium, where the NMs interact before and during application into plants.

This understanding's benefits are the potential application in the agricultural sector that can enhance agricultural productivity with low input of cost and energy, avoiding risks and toxic effects in humans' environment and health. Nevertheless, it is necessary to further studies and follow specific methodologies to englobe the total effects of the diverse NMs over a specific type of plant to generate safety protocols of use, application, and disposal. New research every day is presented to fulfill the necessity of knowledge about the effects of the NMs over the different environments surrounding the plant, such as the soil, water, and microbiota. It is hoping to seek the benefits of using the NMs and avoid any damage to the environment and human health in future years.

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Nanotechnology for Pest and Microbiological Control

Wisam Mucharrafie Hamzah, Irlanda Grisel Cruz Reyes, and Jorge A. Mendoza Pérez

Abbreviations

ATP	Adenosine triphosphate
ASTM	American Society for Testing and Materials
CFU	Colony forming units
DES	Deep eutectic solvent
DNA	Deoxyribo nucleic acid
EG	Ethylene glycol
EO	Essencial oil
FAO	Food and Agriculture Organization of the United Nations.
FTIR	Fourier transform infrared spectroscopy
HLB	Hydrophilic–lipophilic balance
ILs	Ionic liquids
MALDI–TOF MS	Matrix-assisted laser desorption ionization–time of flight mass spectrometry
NADES	Natural deep eutectic solvent
NADEF	Natural deep eutectic fluid
NADEF–CuO	Natural deep eutectic solvent with copper oxide
NMR ^{13}C	Carbon 13 nuclear magnetic resonance
NMR ^{1}H	Hydrogen nuclear magnetic resonance
NPs	Nanoparticles
δ	ppm (signal displacement symbol in nuclear magnetic resonance)

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1 Pest Problems and Their Control in Mexico

As the population increases, the demand for food and other inputs is increasing, so one of the greatest challenges for agricultural researchers is to innovate technologies that generate enough quantity and quality of food to supply the population, as long as they do not degrade health of ecosystems and soils.

Fried, Chauvel, Reynaud, and Sache carried out studies in 2017 that revealed that between 10% and 40% of agricultural products are lost worldwide due to pests of different crops, and therefore, annual losses of 248 billion dollars are generated in world agriculture according to the FAO (Fried et al. 2017).

Therefore, pests not only affect agricultural production, but also affect the quality of crops, which has been generating agricultural insurance. As a federal government company in the field of agricultural insurance, AGROASEMEX, in 2018, reinsured more than 50% of the agricultural area, that is, 1.2 million hectares through 313 Insurance Funds distributed in 29 states, for an insured sum of 25,420 MP. The main crops insured were: corn, wheat, and sorghum. The Parastatal company affirmed that the prevention and control of pests is of the utmost importance to have healthy and sufficient crops. Among the most harmful pests for farmers, the following stand out: the yellow aphid, the white fly, the red weevil, the red spider, the blind man's beetle, the fruit fly, and the leaf miner larva (Abdellatif et al. 2016).

To try to avoid large losses and improve harvests, farmers are using excessive use of synthetic agrochemicals, which generates contamination, such as deterioration of soil health, generating problems related to waste management, among others (Kashyap et al. 2015).

1.1 How Different Pests Affect Crops

The different varieties of aphids affect crops ranging from potatoes, tomatoes or chili, to cotton. This pest stops the maturation process of crops, in addition to being able to transmit a large number of viruses. The beetles known as blind hens can affect the growth and cause the death of different types of crops, such as corn or sorghum, since they feed directly on the roots of these plants (Abdellatif et al. 2016).

2 Nanotechnology Potential in Agriculture

Agricultural scientists are currently facing a great challenge about stagnant crop yields, a large decrease in organic matter in soils, multinutritional deficiencies, and, last but not least, water scarcity (Shiva 2016). To deal with all these problems, nanotechnology finds a solution (Echegoyen and Nerín 2013). This is to preserve the plants from attack by pathogenic microorganisms and generate nanosensors that allow the detection and delivery of the necessary amount of nutrients and pesticides (Ghormade et al. 2015). Different metal nanoparticles such as copper (Cu), iron (Fe), zinc (Zn), silver (Ag), titanium (Ti) among others, are used in agriculture and food industry due to their antimicrobial properties. For example, titanium dioxide is a food coloring that can create a protective barrier in packaging (Zhang et al. 2008). In the case of oilseeds and crop plants, Adhikari et al. (2016) found a positive effect when observing that zinc nanoparticles can penetrate the seed coat and favorably stimulate physiological and biochemical responses. As another example, silver nanoparticles, due to their properties, are used as antimicrobial agents and are used in packaging lines and surfaces destined to come into contact with food (Echegoyen and Nerín 2013).

Structured organic nanoparticles, such as micelles, vesicles, liposomes, dendrimers, biocapsules, among others, have been used as encapsulation vehicles for antimicrobial agents to protect against pathogens and improve the nutritional value of foods and subsequently for the gradual or controlled release of drugs (Perni et al. 2015).

Nanoparticles can penetrate plant tissues when applied to plant leaves in the form of aerosol or spray (Wang et al. 2013), entering through the stomata and thus moving through the phloem toward different plant tissues (Jalali et al. 2017). On the other hand, there is another way to penetrate the plant tissues and that consists of applying it to the root zone by irrigation, and in this way, the nanoparticles can move through the conductive xylem system (López-Moreno et al. 2016).

Another positive point is that some results reveal that only 14.7% of the nanomaterial applied to plants are lost when using the spray or aerosol technique; compared to conventional techniques, they have a 32.5% or more loss (Hawthorne et al. 2014).

Copper nanoparticles, as well as being a very abundant semiconductor metal on the planet, have excellent antibacterial properties (Carrillo et al. 2016; Shende et al. 2015). Copper has greater interest over other antimicrobial metals, because it has a broad spectrum of action against fungi and phytopathogenic bacteria (Lira et al. 2015; Betancourt et al. 2014). The ability to accept or donate electrons is responsible for the antimicrobial properties of copper, as it has a high level of catalytic oxidation and a high potential reduction. When copper is in a high oxidation state, it is highly effective as an antimicrobial due to the interaction with nucleic acids, enzymatic active sites, and membrane components in cells that cause damages (Cioffi et al. 2005). The antibacterial effect of silver nanoparticles is caused by damage in membranes, mitochondria, cellular organelles, nuclear DNA, as well as the production of reactive oxygen species, which are generated when nanoparticles move into the interior of cells (Lira Saldivar et al. 2018). Despite its favorable bactericidal properties in water treatment, one of the disadvantages of silver nanoparticles is that it has been verified by transmission electron microscopy (TEM) images, the damage they could cause to the cell membrane and some elements of the cytoplasm of human cells.

2.1 Crop Plants and Nanotechnology

Nanotechnology has been successfully applied in various fields of technology, mainly in materials sciences, electronics, biotechnology, and medicine. The importance of nanotechnology in the development of new materials was highlighted when it was discovered that size can influence the physicochemical properties of a substance (Shin et al. 2015). Nanotechnology has improved biotechnology allowing that life sciences have significantly broadened the application of nanomaterials in new scientific fields. Applications for nanoparticles include wastewater treatment, environmental remediation, solar energy use, food processing and packaging, development of process industries, medicine and drug formulations and high specificity smart sensors (Prasad et al. 2017a, b). They are also used to study plant metabolism, as well as to enhance plant growth.

Crop plants are the main producers of food and responsible for the balance between ecosystems, supporting the production of organic matter using solar energy (McKee and Filser 2016). Nanoparticles induce morphological and anatomical changes in plants, with positive or negative affection over their growth and development. When plants are exposed to nanoparticles, they penetrate the cell wall and cross the cell membrane through the pores using a size-specific transport mechanism to reach the absorption system of the plant, where the nanoparticles are distributed and translocated. The effect of NPs on plants varies from one species to another and the efficacy of NPs depends on their concentration and size. Plants require different macro- and micronutrients in several concentrations for their normal growth and development. The nutrients are in the soil, but sometimes, some of these nutrients are not available to plants or present in very low amounts. Replacing this nutrient deficit adding nanoparticles can be used as a modern agriculture strategy.

2.2 Use of NPs in the Management of Plant Diseases

Application of nanotechnology in the treatment of plant pathology is a novel approach. The action over the physicochemical properties of several substances and the ultra-small size of the nanoparticles allow them to be used as phytoenhancers but also as phytopathogens. NPs have great potential to protect agricultural products from bacteria, fungi, and viruses. Bacterial agents and pathogenic fungal species are known to attack a wide variety of plants, causing decomposition of vegetables and crop losses. Some other organisms can be highly specific, but are the less. The application of NPs with existing pest control protocols can help improve plant protection. Several authors have reported that silver ions (Ag^+) block fungi and bacteria enzymes that metabolize oxygen to sustain their aerobic metabolism, leading to suffocation and resulting in death for both species (Abd-Elsalam and Prasad 2018). Nanoparticles offer large specific surface area and, therefore, a higher affinity for the target organism acting as nanopesticides. These nanopesticides can help increase the dispersion and wettability properties of agricultural formulations (Bhattacharyya et al. 2016). Metallic NPs can be used as highly effective nanopest controls against plant–pathogens, such as insects and pests due to their smaller size and high reactivity, which can affect the activity of those organisms. Metallic silver does not present antimicrobial properties, but silver NPs act as antimicrobial agents. Silver nanoparticles shown synergistic activity when combined with drugs designed with pathogenic activity against fungi and yeasts (Jogee et al. 2017).

3 Nanopesticides

Pests and diseases have affected agricultural production, since elder times limiting profits and inducing significant impacts on farmers income. Damage occur in field crops and during storage. Synthetic pesticides are used to manage pests and increase crop yields and protect from insect-borne diseases in stored products, with high risks to workers, consumers, and the environment. Almost 2.5 million tons of pesticides are used on crops each year and the global damage caused by pesticides reaches billions of dollars, annually. Nanotechnology is proposed as a new promising area, ready to avoid the dangers of chemical pesticides, which could play an important and effective role in the control of plant pests and diseases. Nanotechnology offers great promise in the development of new formulations called nanoformulation, for innovating products including nanopesticides, especially with the application of nanoparticles as an alternative auxiliary factor in the preparation of pesticides (Abdellatif et al. 2016). New formulations can improve the effectiveness and stability of insecticides and offer to provide a controlled release of the molecules at the site of action with the ability to release the active compound in a specific target organism (Prasad et al. 2019).

3.1 Nanoformulation

New advanced research have developed different types of nanopesticides, such as: nanocapsulated formulations, nanoemulsion, nanogel, nanospheres, and nanoparticles of metal and metal oxides. New nanopesticides are prepared using nanostructured molecules with pesticidal properties and adding very small particles with pesticidal active ingredients. Nanoformulations help to increase the apparent solubility of a poorly soluble active ingredient or to release the active ingredient in a slow or targeted manner, thus protecting the active ingredient against premature degradation.

4 Nanopesticide Release Processes

Nanomaterials used to formulate nanopesticides have enhanced properties, such as biodegradability, solubility, permeability, and thermal stability. Nanoparticles, designed to interact with the active ingredients of pesticides, often show a broad spectrum of activity against plant pests and pathogenic diseases. Nanoparticles often exhibit novel characteristics such as greater stability, more chemical reactivity, and possess high electrical conductivity. Pesticide release can be done by adsorption on nanomaterials as a carrier, encapsulation in a nanoparticulate shell, entrapment in polymeric nanoparticles, and binding of NPs mediated by different ligands. The ability to delay or control the release of pesticides in target organisms is achieved by these nanopesticide delivery methods (Singh et al. 2015). Controlled release technology has emerged as an alternative approach with the promise of solving the problems that accompany the use of some agrochemicals while avoiding potential side effects with others. Inorganic metallic nanomaterials have the ability to cross the cell membrane to interact with internal structures and lodge within the membrane. Some of them affect the regulation of solute movements, protein exchange, and cell recognition. Biochemical reaction mechanisms involve the disruption of multiple cellular mechanisms and the response to oxidative stress in eukaryotic and prokaryotic cells. After entering the cell, the ionic nanoparticles intercalate with the DNA or RNA, consequently inhibiting the proliferation and replication of the pathogen and finally killing the cell. The antimicrobial activity of the nanoformulation depends on the structures, size, and concentration of the nanoparticles.

5 Phytochemicals in Nanoformulations

Several phytochemicals extracted from different parts of plants such as essential oils, alkaloids, flavonoids, glycosides, limonoids, saponins, and phenolic compounds become promising tools such as fungicides, bactericides, and nematicides. Essential oils contain volatile terpenes and compounds such as phenolic compounds which have insecticidal, bactericidal, viricidal, fungicidal, antiparasitic, and nematicidal activities with different mechanisms of action and other medicinal properties (Elgengaihi et al. 2016). Nanoemulsified systems where essential oils (EO) are encapsulated have potential application in nanopesticide products for antimicrobial delivery systems that provide liberated control. A variety of EO delivery systems have been developed in two categories of nanocarriers: (1) polymeric nanoparticle formulations, which resulted in a significant improvement of the antimicrobial activity of the essential oil, and (2) lipids transporters including liposomes, solid lipid nanoparticles, nanostructured lipid particles, and nanoemulsions. Nanoemulsions are colloidal nanodispersions of oil and water that are thermodynamically stabilized by an interfacial surfactant/cosurfactant layer. Surfactants reduce the surface tension between the oil and water interfaces and are essential for a stable droplet size. Most EO nanoemulsions are currently prepared with synthetic (non-ionic) surfactants, because ionic (polymeric) surfactants are generally not preferred due to toxicological effects.

5.1 Nanoemulsions and Polymer-Based Nanoformations

The controlled use of agrochemicals could also be possible through the development of a smart management system using biomaterials. There are controlled release formulations of agrochemical pesticides that use amphiphilic polymers in the nanorange. Polymer-based nanoformations have been used for encapsulation of most insecticides. Different polysaccharides like chitosan, alginates, and starch, and polyesters like poly-ε-caprolactone and polyethylene glycol, have been considered for the synthesis of nanoinsecticides. Encapsulation of various agrochemicals in chitosan, silica, alginate, and calcium carbonate is an option for controlled and sustained delivery (Choudhary et al. 2017). Biomaterials as components of the nanoparticle system can reduce the risk of dangerous agrochemicals for the improvement and protection of crops. Nanoparticles prepared from natural sources and biopolymers have a broad spectrum of biocompatibility and biodegradability. Methods involved in nanoemulsion preparation include high energy processes: homogenization and high pressure ultrasound and low energy processes: phase inversion temperature and emulsion inversion point. The high energy processes use mechanical devices to produce disruptive forces to break up the oil and water phases to obtain nanoemulsions. The low energy method uses stored internal energy to form tiny droplets. Emulsions are obtained by changing the process parameters such as temperature, composition and others that affect the hydrophilic–lipophilic balance (HLB) (Nirmala and Nagarajan 2017).

5.2 Bioactive Nanopesticides

Biocontrol agents are natural enemies of pests and pathogens, and they could also play a role as biopesticide products. There are some biological control agents such as entomopathogens, rhizobacteria, endophytic microbes, fungi (entomopathogens), bacteria (rhizobacteria), viruses, and nematodes (entomonematodes) that are used against insect pests and disease pathogens. Mycopesticides (fungal biological control agents) are promising biological pesticides, as they do not need to be ingested; instead, they act by contact, and they are very specific and can be easily mass produced. Microbial products such as enzymes, antibiotics, inhibitors, and toxins also showed promising as biopesticides against plant–pathogens and pests (Bhattacharyya et al. 2016). Phytosanitary products containing nanomaterials that alter the functionality or risk profile of active ingredients (nano-enabled pesticides) promise many benefits over conventional pesticides, such as better targeting of pest species, higher efficacy, higher application rates, and higher environmental safety (Walker et al. 2017).

6 Nanocoatings

Nanocoating is a unique method of modifying the surface properties of a matrix, which makes the matrix adapts to the environment, where it is deposited and can extend its useful life. The nanocoating can be defined as a thin film (a few nanometers thick) formed or deposited on the surface of a component made of another material, which is similar or not the mechanical properties of the matrix and generally has good corrosion resistance and wear resistance (Gu et al. 2020). At the same time, due to the influence of the surface effect, the effect of their small size and quantum-like effects, nanomaterials exhibit many different characteristics from macromaterials in physical properties and mechanical properties. The ASTM E2456-06 standard defines nanoparticles as "a sub-classification of ultrafine particles with lengths in two or three dimensions greater than 0.001 μm (1 nm) and smaller than about 0.1 μm (100 nm) and which may or may not exhibit a size-related intensive property" (ASTM 2008). The most notable change in the material properties at the nanometric scale is due to the increase in the surface area caused by a reduction in the particle size of the material. Nanocoatings are focused to generate film barriers to provide an opportunity to enhance a kind of protective packaging. The main attraction of nanocoatings or films is its high barrier properties provided by its nanostructured network and its low permeability to gases (for instance, water vapor and oxygen).

Organic/inorganic nanocoatings refer to the composite of organic nanomaterials and inorganic nanomaterials to form coatings, including dispersion of inorganic nanoparticles into organic substrates. In the whole system, a phase is called matrix and is a continuous phase; the other phase is a reinforcing material and belongs to the dispersed phase. Organic/inorganic nanomaterial coatings combine the properties of inorganic particles and organic polymers under the combined action of the two, generating better performances in the mechanical, electrical, thermal, and optical aspects of the materials. Therefore, this kind of new material combines many characteristics of inorganic, organic, and nano, and it has a better performance as a structural material. The fundamental purposes of nanocoatings are to prevent physical, chemical, or microbial degradation and to avoid the loss of its properties while at the same time maintaining the quality of the coated product during its extended shelf life. However, nanocoatings must be designed as biodegradable, renewable, and compostable (Jambeck et al. 2015). Nanocoatings are classified as passive and active, with intelligent design and smart according to their interaction with different products.

6.1 NADES

Deep eutectic solvents (DESs) are improved successors for the green solvents: ionic liquids (ILs) with similar physicochemical properties but different components. DESs have attract considerable interest in related chemical research, based on the superiority of DESs over ILs and in the preparation of membranes or coating compounds on porous materials (Li et al. 2018).

When the compounds that form a Deep Eutectic Solvent (DES) are abundant in natural components, such as sugars (glucose, sucrose, fructose, etc.), alcohols, amino acids, organic acids (lactic, malic, citric acid, etc.), urea, and choline derivatives, they are called natural Deep Eutectic Solvents (NADES) (Bajkacz and Adamek 2017). When viscosity of NADES is modified, it can be generated as a fluid material or natural deep eutectic fluid (NADEF).

The NADES offer infinite opportunities in the development of process, with prospects for improvement in different steps and sub-steps of processes and can be applied in different fields of research, particularly as solvents for extraction and synthesis, catalysis, gas separation films, coating materials, and electrochemical materials. NADES are truly designed solvents that can be used as means of extraction or separation of contaminants as well as being sustainable and safe (Martins et al. 2014).

This capacity can be used in the modification of materials, such as polymers and silica, which are used as membranes in the extraction and separation of pollutants (Shende et al. 2015).

6.2 Synthesis of NADEF–CuO

For the synthesis of NADEF, sucrose was dissolved in 3 mL of ethylene glycol at 65 °C for 2 h and kept under vigorous stirring for 24 h, then 1.35 g of sodium acetate was added, and the temperature was incremented to 80 °C for 3 h, and all the previous operations have been taken under reflux conditions. The product of the reaction was a brown-looking solvent. Viscosity was increased using a 2-L air stripping system with a clean air current at 80–85 °C during 12 h. 0. Copper oxide nanoparticles (Sigma-Aldrich nanopowder, 25 nm particle size, TEM) were added directly to the NADEF solution (30 ug/100 mL of NADEF) and stirred 4 h at 300 rpm. Also copper oxide nanopowder was dispersed using a sonication process with a high-intensity Vibra-Cell VCX 750 ultrasonic processor (Sonics and Materials, Inc., Newtown, CT), employing 20 kHz at 35% amplitude. An acoustic power of ~0.5 W/cm^3 was applied for 5 min × 5 times.

6.3 Characterization of NADEF–CuO

In the characterization studies, viscosity studies were performed using Rheometer MCR-502 of Anton Paar. The dynamic light scattering studies of the NADES of sucrose/ethylene glycol and copper were analyzed with a Dispersor Nano Zetasicer 5, Malvern. For the nuclear magnetic resonance (NMR) studies, the proton (^{1}H) and carbon (^{13}C) NMR spectroscopies were obtained, and the NADES were recorded using an Agilent 400 MHz 54 mm NMR DD2 in D_2O in dimethyl sulfoxide (DMSO) as standard. Fourier transform infrared spectrometry (FTIR) were carried out in a Horiba, IR2 Module with a resolution of 10 cm^{-1} in a spectral range interval of 500–4000 cm^{-1}. Mass spectroscopy studies were performed with a Bruker Daltonics MALDI–TOF MS.

Cotton textile sheets (2.5 cm × 2.5 cm) were alternately deposited using a multi-vessel automated dip coater system (KSV NIMA, Finland) on NADEF–CuO solution to form 5–10 bilayers. It was required to dry the cotton sheets during 30 min at 60 °C in order to avoid fluidization of the nanocoating.

6.4 Experimental Results and Discussion

The results of NADES of sucrose/ethylene glycol/copper oxide have a viscosity of 0.1 Pa·s and a decomposition temperature of 110 °C. In the studies of dynamic light scattering for the NADEF–CuO particle, size ranges from 79 to 164 nm, with an average particle size d_{50} of 92 nm. Figure 1 shows the FTIR for the synthesis of the NADEF–CuO. It has been added the spectra from sucrose and EG for comparison

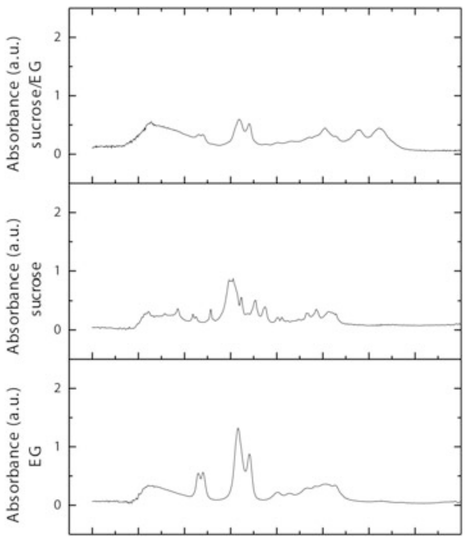

Fig. 1 Spectrum FTIR of NADEF–CuO

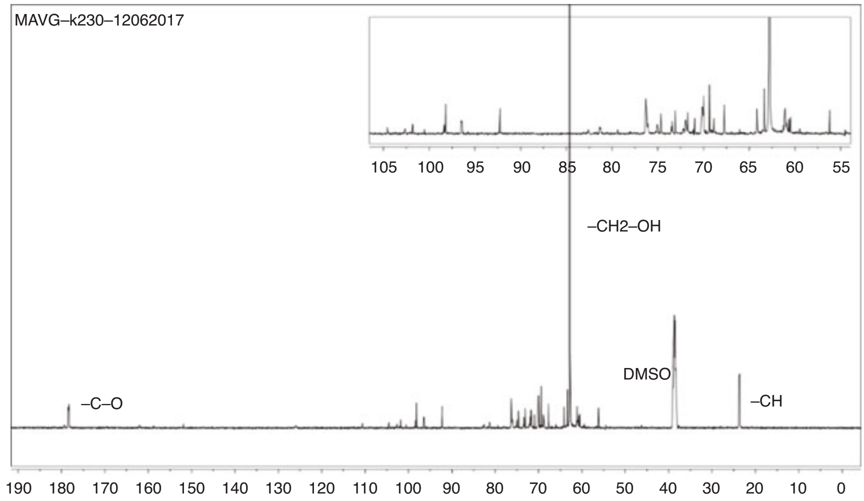

Fig. 2 Spectrum NMR of ^{13}C of NADEF–CuO

purposes. For sucrose, it can be observed the characteristic bands corresponding to sucrose at 1053 cm^{-1} tension glycosidic bond, the bands between 881 and 857 cm^{-1} are associated with links C–O and C–C of stretching, the 1636 cm^{-1} signal corresponds to the presence of an OH^{-}– of tension characteristic of fructose, at 1430–1199 cm^{-1}, there are the bonds O–C–H, C–C–H, and C–OH groups, which are the vibrational bands of carbohydrates, and at 1348 cm^{-1}, it is observed the vibrational mode of nodding –CH_2. For the ethylene glycol (EG), the band corresponding to the hydroxyl group (O–H) at 3304 cm^{-1} and the stretching of C–H at 2931 cm^{-1} and 2874 cm^{-1} of the –CH_2 and –CH_3 groups are observed. The most important about Fig. 1 could be the presence of ethylene glycol in the NADES to 1406 cm^{-1} while to 1558 cm^{-1} is observed the link of sucrose, EG, and acetate de sodium, by last to 1642 cm^{-1} was observed a displacement which it could be at the breakdown of the sucrose molecule and the union of EG with the glycosidic bond of fructose and glucose by Van Der Waals forces.

For NMR studies, the samples were prepared using dimethyl sulfoxide (DMSO) as a solvent. The ^{1}H and ^{13}C NMR studies of NADEF–CuO were performed and the carbon spectrum (Fig. 2) corroborated specifically the product formed in the reaction. In this spectrum, there are signs of δ188 corresponding to carbonyl groups, there is also a very strong signal at δ63 of the presence of alcohol groups that correspond to those belonging to ethylene glycol, and in the same way, δ24 are signals belonging to group –CH.

MALDI–TOF MS results for the NADEF–CuO samples were performed at the conditions of 180 °C and 0.4 bar pressure (Fig. 3)

In Fig. 3, there is a total molecular weight of 347.093 g/mol corresponding to the molecules formed in the synthesis of the NADEF–CuO. This molecule disintegrates in two molecules (–CH_2–OH) losing half of its molecular weight, observing signal

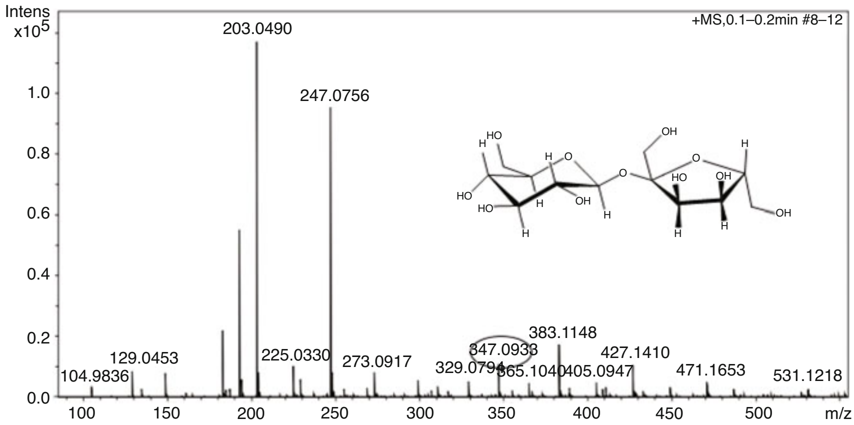

Fig. 3 Mass spectrum of NADEF–CuO

Table 1 Results for quick test of bactericidal and fungicidal effect with nano-coated cotton textiles

Sample ID[a]	Bacteria CFU (mean value × 10^6)	Fungi CFU (mean value × 10^4)
Nano-coating sheet	0.8 ± 0.04	0.4 ± 0.05
Control sheet	1.2 ± 0.15	0.8 ± 0.1
Blank	1.0 ± 0.03	0.6 ± 0.04

[a] All the test were performed by triplicate

273.09, also later the loss of a molecule of ethylene and acetate can be observed which are in the alpha position of the carbons which it makes them very unstable and tend to be the first outgoing groups. The product sucrose/EG has a molecular weight of 405.10 g/mol; in addition, we have two signals 247.0756 and 203.0490 and we have two and three molecules of methyl group (–CH_2), while at 273.0917, there is the loss of two molecules of CH_3–OH.

Quick tests of bactericidal and fungicidal effects with the nano-coated cotton textiles were carried out by placing fruit and vegetable residues (as a crop reference) inside Petri dishes with agar gel. The crop residues were placed over the textiles. In addition, control Petri dishes were prepared without the nano-coated cotton textiles (Blank) and others with a textile sheet but without the nanocoating (Control sheet). After 12 days at 30 °C, the gels were scraped and the CFU of bacteria and fungi were quantified (Table 1).

Results in Table 1 indicate that effect on NADES–CuO nano-coating inhibits the growth of bacteria and fungi. This allows establishing that with the NADES–CuO coating, an effect is being obtained to control opportunistic microorganisms that can develop in vegetable and fruit crops.

7 New Developments: Nanofungicidal in Clothes and Medical Wound Heal Materials

The use of antifungal sheets is to generate a tool for the development and application of copper nanoparticles, in order to obtain a sheet and/or a cotton fiber with a coating with nanoparticles. Since one of the biggest problems in the community is the pests that agriculture generates, one of these is fungi, bacteria, and microbes.

7.1 Method of Impregnation, Drying, and Curing (Pad-Dry-Cure Method) in Cotton Fibers

Cotton is considered the "King" of fibers, since most of the clothing manufactured in the world is made of cotton. This fiber has a very good resistance, and is considered to provide comfortable fabrics due to the fiber's good moisture absorption and its absorption or drainage properties. Since cotton fiber has wide applicability (garment manufacturing, medical implement manufacturing, protective clothing manufacturing, etc.), it makes cotton fabric an excellent candidate as a textile substrate for the development of functional fabrics with notable improvements, such as antimicrobial properties (Yafa 2006).

The pad-dry-cure technique is the conventional technique for applying finishing products to cotton fabrics. It is a simple and easy technique. The cotton material is immersed for 5–10 min in the aqueous solution that contains the nanoparticles, then the fabric is padded through pressure rollers to provide a certain moisture uptake, and after that the fabric dries and cures for a specified time and at a specific temperature (Wakelyn et al. 2007).

7.2 Exposure of Crops to Different Pollutants

In the experimentation, four (4) crops were exposed to food residues and soil, two of them with cotton textile with an adhesion (nano coated) treatment of copper oxide nanoparticles with the aforementioned method and the other two with pure cotton without any type of treatment, in order to notice what would happen with microorganisms growth during several days.

After 2 weeks in a dark environment at room temperature (22 °C), the four crops with soil and food contaminants were analyzed. The first day did not generate changes, but in the next 3 days, microbial and fungal growing in crops began to be noticed, especially in the food, due to their decomposition. Also it began to be observed a change in the crop and the least significant changes showed was the experiments that contained soil.

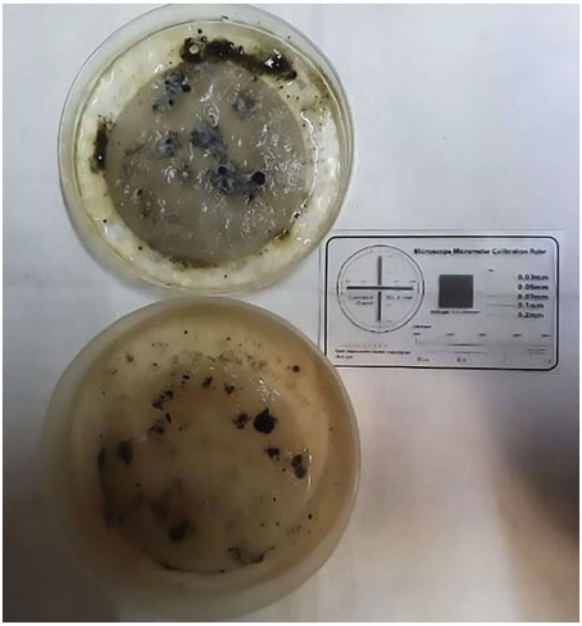

Fig. 4 Qualitative analysis of antimicrobial testing of copper oxide in soil

As can be seen in Figs. 4 and 5, the cotton textile nanocoated with the copper oxide nanoparticles did not generate bacterial culture streaks compared to the other petri dish without the copper oxide nanoparticles, and it generated bacterial culture streaks with an approximate diameter at 30 mm.

8 Conclusions

Plant protection products containing nanomaterials that alter risk profile of active ingredients (nano-enabled pesticides), enhancing protective effects, promise many benefits over conventional pesticide products, such as increased efficacy, lower application rates, and higher environmental safety. Nanoparticles can stimulate plant growth and development and effective plant protection with reduced negative environmental impact. Nanotechnological has advanced developing new nanoformulations in order to reach more benefits, for example, using nanocoatings with "smart" delivery to prevent plant diseases is an environment-friendly option to be used for plant disease management. Some potential biomaterials useful for preparation of effective and safe nanoformulations should be considered and supported by researchers and the industry in the future. For example, NADES combined with metal oxides or pesticides could enhance crop management and open great opportunities to new agrotechnology developments, like the proposed in this chapter: nanofungicidal in clothes and medical wound heal materials.

Fig. 5 Culture with and without copper oxide nanoparticles with food residues, in order to make the corresponding comparison

Finally, this chapter establishes that it is very important to know each one of the characteristics of the nanomaterials developed and working in this way that it can be obtained precise and specific knowledge of their properties. Using copper oxide nanoparticles is a great alternative to end pest and microorganism health-related problems in crops as long as we have a good management of nanocoating process, but as other proposals, this technology will have its advantages and disadvantages.

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Part IV
Nanoremediation

Nanoremediation

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Abbreviations

Cd	Cadmium
As	Arsenic
Pb	Lead
Cr	Chromium
Zn	Zinc
Hg	Mercury
μg	Micro gram
m	Meter
NPs	Nanoparticles
Fe^0	Zero-valent iron
E°	Standard reduction potential
ROS	Reactive oxygen species
eZVI	Emulsified zero valent iron

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1 Introduction

A few worldwide issues are compromising the life on the earth inclusive of environmental contamination, climatical change, soil securities, food securities, energy, and so on. The filthy environment (viz. soil, air, water, etc.) could likewise be contemplated as an arising issue (Belal and El-Ramady 2016; Lodeiro et al. 2016; Ibrahim et al. 2016; McCrink-Goode 2014). These contaminants could be emanated from various resources inclusive of industrial exploits, traffic, agricultural activities, and mining activities (El-Ramady et al. 2017). The contaminated terrains suffered from highly concentrated toxic pollutants annihilating agroecosystem (Stiborova et al. 2017). These toxic degrees of contaminants confine the maintainable regulation and controlling pollution in those terrains (Stiborova et al. 2017; Tripathi et al. 2015). Thus, a worldwide cooperation between various nations ought to be built regarding worldwide pollutions (Günther and Hellmann 2017).

Worldwide crop production was and still insufficient for feeding all population all over the globe (Sala et al. 2016; Fraser et al. 2017). There is an important gab in between worldwide food productions and the consumptions (Sandström et al. 2017; Sundbo 2016; Dandage et al. 2017). Subsequently, all nations ought to attempt to plan a coordinated production scheme in order to form the food energy water unification (Hang et al. 2016; Kucukvar and Samadi 2015; Peterson 2017; Smajgl et al. 2016). Thus, some arising resolutions ought to be routed for determining worldwide food emergency inclusive of biotechnology as a few nanomaterials have been produced with an objective to utilize as a nutraceutical, as well as active drug components and nanotechnology (El-Ramady et al. 2017).

Subsequently, the elimination of contaminants from water and soil might be connected with manageable remediation as well as energy productions (Zheng and Shi 2017; Kovacs and Szemmelveisz 2017). Numerous techniques for integrated and viable administration of contaminated terrains ought to be tended relying upon a few variables such as kind of contaminants and their extent, the intention behind the land utilization after remediation methods, characterization of soils along with its topography, climatic as well as cropping patterns, and resource accessibility with their economic status (Pandey et al. 2016a; Saha et al. 2014).

Nanoparticles are the utmost significant approach toward remediation of the polluted atmospheres. These remediations for various ambiences utilizing nanomaterials or nanoparticles commonly entitled as nanoremediation (Kuppusamy et al. 2016; Jain et al. 2016; Gil-Díaz et al. 2016; Wang et al. 2017; Gomes et al. 2016). This nanoremediation can be accomplished in the emergence of nanomaterials and/or nanoparticles utilizing plant or phyto-nanoremediation, animal or zoonanoremediation, microbe or microbial nanoremediation (El-Ramady et al. 2017). Therefore, there is a pressing requirement for controlling environmental pollutions under a viable regulation (Cai et al. 2016; Abhilash et al. 2016). Diverse uses of nanomaterials or nanoparticles have been employed in numerous segments inclusive of sustainable crop productions (Tripathi et al. 2016), reduction in nutrient loss, disease suppression, and crop yield upgrade (Shalaby et al. 2016; Ditta et al.

2015). Nanoremediation for sustaining crop productions in contaminated terrains ought to be overseen in an appropriate manner since the extension in such contaminated terrains for agricultural productions (Panpatte et al. 2016; Patil et al. 2016; Kuppusamy et al. 2016). This at present came about because of the trouble in estimating the sustainable crop productions in such contaminated terrains along with dearth in assessing procedures for execution of phytoremediation in a bioeconomic frame (Tripathi et al. 2016; Shalaby et al. 2016). Hence, the object of this chapter is to assess nanoremediation and its technique in contaminated terrains looking for sustaining crop productions. Nanotechnologies and their utilization in controlling pollutions, inclusive of environmental pollutions and its viable managements, will additionally be enlightened.

2 Environmental Pollution

Environmental pollution is a significant worldwide labyrinth nowadays (McCrink-Goode 2014). These pollutions happen in water, soil, air, and ecological systems. Environmental contamination incorporates various appearances (Awasthi et al. 2016), for example, inorganic and/or organic pollutants; however, the utmost significant and recent kinds are the electronics wastes and nanomaterial and/or nanoparticle contaminants (Li et al. 2016; Ibrahim et al. 2016). The usual contaminants incorporate heavy metals, pharmaceutical pollutants, organic pollutants, aromatic polycyclic hydrocarbons, and xenobiotics volatile organic compounds (Liu et al. 2016; Zhou et al. 2015; Kenessov et al. 2016; Oiamo et al. 2015; Witczak et al. 2016). Developing as well as developed nations experience the environmental pollution and its effects. Therefore, newer approaches ought to be developed to recognize and screen notable poisons as well as various newish toxins (Lodeiro et al. 2016). Various contaminants ought to be taken out from various environments like water, soil, air and ecological systems by applying diverse remediation technologies.

Day-to-day colossal contaminants and/or xenobiotic components are being expanded in ecological systems impressively. Environmental contamination these days is viewed as a significant issue for human as well as environment (Pandey et al. 2016b; Araújo et al. 2015). The environmental contamination could be characterized as any release of energy or material within naturalistic origins (like, soil, water, forest, air, so forth) executing or might execute chronic (long term) or acute (short term) harm to earth (Araújo et al. 2015). Different pollution resources or numerous synthetic components that address those resources include: (1) natural operations (saline seeps and geological erosion), (2) human exploits (mining and constructions), (3) industry instigated operations, (4) agriculture instigated operations (pesticides, composts), (5) acetous depositions, (6) radioactive waste, and (7) pharmaceutical wastes (Araújo et al. 2015).

Regarding soil contamination, it is vital to screen and remediates distinctive harmful contaminants in the soils in view of universal food safety. Because of the intricacy and elements of the soils, it is addressed as sink and additionally the resource of impurities that could be detected in swapping with water, air, and biosphere (Kenessov et al. 2016). Consequently, the features of soils could be utilized as a great indicator for contaminant soil, for example, soil data, soil basal respirations, soil microbial communities, and so on (Chen et al. 2016; Romero-Freire et al. 2016; Azarbad et al. 2016). Four requirements are essential to measure soil contaminations, for example, assessment of spatial and temporal trends of pollutants concentration, efficacy development of soil remediating technology, determining contamination resources and soil map for contaminated lands, and verifying that soil qualities fulfil the safety specifications (Kenessov et al. 2016).

Concerning water contamination, it has drawn several researcher's attention. Various resources of water contamination have been described which includes industrial resources (pharmaceutical, petrochemical, plastics, leather, textile, dye, food, paper industries, and so on), agronomic operations (like pesticides and composts), municipality waste water, and so on (Zhou et al. 2015). Subsequently, various types of water corpus might be experienced contamination hazards, including river water, ground water, sea water, waste water, and so forth (Singh et al. 2016; Sharma and Malaviya 2016; Lyubimova et al. 2016; Effendi 2016; Zeng et al. 2016). Diverse water pollutants could cause extremely hazardous health-related issues, like mutagenicity, carcinogenicity, embryotoxicity, reproductive system-related issue, and dysfunction of liver, kidney, brain, and central nervous system (Zhou et al. 2015).

Air pollution is the usual issue in industrial territories because of the pollutants that come out of different industries. The main toxins in air incorporate heavy metals [like cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), zinc (Zn), and mercury (Hg)], chlorofluorocarbons, hydrocarbons, carbon monoxide, nitrogen oxides, sulfur dioxide, organic chemicals (like organic volatile components), and particulate elements (Ingle et al. 2014). This is very much archived that the impacts of air contamination on the human hygiene are treated as a severe problem. Various techniques have already been utilized in perceiving this connection between air pollution and human health, which inclusive of time-series experiments, fixed-effects or panel experiments, cross section and cohort-instigated experiments, and lastly natural experiment-based experiments (He et al. 2016). A few researchists affirmed the higher and greater level of air pollution in developing nations than developed nations (He et al. 2016; Ebenstein et al. 2015). It has been discovered that the peripheral air contamination level is higher in various Asian nations, where average yearly fine particulate matter (finer inhalable particles $PM_{2.5}$, with breadth generally 2.5 μm) in Beijing is 85.9 $\mu g/m^3$ compared to the yearly mentioned level by WHO, i.e., 10 or 25 $\mu g/m^3$ for 24 h, whereas the European Union diurnal limitation is 50 $\mu g/m^3$ (Selmi et al. 2016; Wu et al. 2016; Kim et al. 2016). By monitoring air pollution levels in many nations, such as China, Japan, United Kingdom, France, Egypt, Belgium, Sweden, USA, Italy, Spain, South Africa, and Canada, it might be inferred that the environmental contamination is a worldwide issue and all nations ought to cooperate in checking and remediating the problem. This environmental contamination incorporates water, soil, and air pollutions that vary from one spot to another spot and from nations to others. Various strategies and newer approaches ought to be followed in order to handle those pollutions by implementing viable management (El Ghorab and Shalaby 2016).

3 Management of Environmental Pollution

Natural resources ought to be managed by utilizing sustainable regulation. Since these are the major sources for our life that supports us with vital food, fiber, feed, and fuel (Shalaby et al. 2016; Akhtar et al. 2016). The perfect resolution for sustaining contamination regulation is preventing the pollutions first or diminishing or controlling it (Ullwer et al. 2016).

Soil contamination in European Union is assessed by greater than 2.5 million contaminated lands presenting around 60% hydrocarbons as well as heavy metals (Domínguez et al. 2016). Numerous anthropological operations, like mining and smelting, industrial wastes, agricultural practices, and so forth resulted in soil pollution (Liao et al. 2016). With respect to managing the soil contamination, it is a massive goal and challenge as well for all nations from the past several years. Numerous strategies have already been implemented to deal with this management relying upon the kind and degree of contamination.

Because of the urbanizing and quick demographic outgrowth, there is an expanding water requirement for all. Because of demographic expansion and economical prolongation, the need for water is successively expanding across the globe, which results in a large volume of waste water. Consequently, an environmental concernment ought to be considered for the management of water contamination or treating in a feasible manner (Cai et al. 2016; Ahmad et al. 2016). Moreover, there is a serious difficulty inside a water allocating system for utilizing water resources adequately for the fulfilment of various purposes without causing a lot of environmental stresses for under water corpus (Zhang et al. 2014; Cai et al. 2016). Subsequently, a few potent conflicts would be manifested in numerous urban areas around the globe because of this expanding crisis and confined aqua resources, especially under the higher dependability on fresh water, which has brought about extreme water deficit in urbane water allocating systems (Cai et al. 2016; Zhang et al. 2014).

It might be noticed the air contamination by collecting all the details about air pollutants in nature and their impacts along with various emissions with different concentrations in the air. Because of the issues brought about via air contamination, human hygiene and the visibility of ecological systems ought to be addressed (Knox et al. 2013). In this way, a few investigations reported exposure to contaminated air result in some negative results like irregular heartbeat, nonfatal heart attacks, diminished lung function, increased respiratory symptoms, and aggravated asthma (Giovanis 2015). Numerous techniques have been embraced around the globe toward sustaining air contamination regulation which vary from one place into another relying upon the kind of air contamination and its extent. These techniques incorporate (1) vegetation in metropolitan zones or utilizing trees, e.g., in Greece, in France, in China, and so forth (Zeng et al. 2014; Sawidis et al. 2012), (2) focusing on air pollution in policies, (3) checking air pollution (Kouddane et al. 2016), (4) identifying resources of air pollutants and pollution, (5) forming small self-sustained metropolis and new policies and/or legislation ought to be embraced, (6) restricting or capping air pollution producers, (7) improving technologies to diminish or eliminate releases, and (8) provide perception concerning health risks to residents. Therefore, the world is confronting a solid challenge of overseeing sustaining air contamination on account of the intricacy of air contamination resources, inadequate funds or resources to monitor and enforce, and social as well as political challenges in characterizing policies to restrict release. Worldwide, viable managements for air contamination cannot be able to remediate and a few stages or techniques must be followed in limiting impacts caused by air contamination (Adams and Kanaroglou 2016).

4 Crop Production in Polluted Environment

Crop production ought to be adequate for feeding all the population across the globe. These adequate propagations are in consummation between the non-food as well as food crops, like horticulture, floricultures, biofuels, and biomasses. From this perspective, a newer strategy regarding the utilization of contaminated terrains in crop propagation is required. Moreover, because 33% of arable spots are polluted already, so utilizing those polluted terrains would be a suitable resolution in neoteric agricultural practices. That implies, utilizing such contaminated territories would result in more and extra difficulties from an environmental perspective. Thus, more appropriate intercessions in the aggrotech division are essential for assuring safety and sustainability of those applicable producing systems (Abhilash et al. 2016; Abbas et al. 2015). It may be inferred that any sustaining crops propagation strategy ought to be deliberated that utilizing arable terrains relies upon the real circumstance for energy, climate changes, water, and soil.

Polluted terrains are viewed as harmful to human hygiene and food security as well. Those terrains ought to be utilized for both environmental and agricultural manageability due to the increasing interest in arable terrains (Abhilash et al. 2016). Subsequently, besides the agricultural productions, there is a need to utilize these contaminated terrains to develop biomass and biofuel crops and biofortifying grains (Edrisi and Abhilash 2016). Another benefit of utilizing contaminated terrains for biofuel crop propagations is to decrease contamination as well as the discharge of CO_2. With respect to plant species which might be propagated for producing biofuel, there are a few plants, like *Jatropha curcas* L., *Arundo donax* L., *Pongamia pinnata* L., *Ricinus cummunis* L., *Populus spp*., *Panicum virgatum* L., and *Miscanthus giganteus* that could be grown in polluted, degraded, and marginal terrains (Edrisi et al. 2015; Edrisi and Abhilash 2016) (Table 1).

Because of the significance of biomass and biofuel production in contaminated territories, like all biological systems, the crop production usually influences by the environmental contamination and its extent. Therefore, it is vital to diminish or

Table 1 Experiments conducted in Cd-contaminated soils for crop production and the accumulated level of Cd in different plant portions

Plant name	Plant parts	Cd levels (mg/kg)	Reference
Zea mays L.	Entire plant	0.89	Ruttens et al. (2011)
	Grains	0.07	Meers et al. (2010)
Spinacia oleracea L.	Shoot	0.05	Ismail et al. (2014)
Ricinus communis L.	Stems	0.43	Irshad et al. (2014)
Brassica napus L.	Entire plant	0.20	Yu et al. (2014)
Chrysanthemum indicum L.	Shoot	7.40	Lal et al. (2008)
Tagetes erecta L.		7.00	
Gladiolus grandifloras Andrews		8.00	
Lupinus luteus L.	Shoot	1.60	Dary et al. (2010)
Prosopis juliflora DC.	Entire plant	0.17	El-Ramady et al. (2017)
Phragmites australis	Shoot	<0.2	Bonanno et al. (2013)

restrain this contamination by viable management. In addition, this pollution is not just compromising crop propagation and their quality yet additionally the worldwide food security. Furthermore, the contaminated terrains could be viewed as a significant resource to propagate energy crops as an incredible strategy and a proper resolution regarding the worldwide discussion about the competitions between food or fuel productions.

5 Nanotechnology in Controlling Pollutions

Nanotechnology has appeared during the 1980s, which is a study to elicit and control an issue at a dimension within 1–100 nm (El-Ramady et al. 2017). This erudition has been performed a significant part intending to various efficient and innovative resolutions for a wider range of environmental challenge (Patil et al. 2016). Therefore, another branch is as of now arose mentioning environmental nanotechnology, which manages diverse remediation techniques utilizing the usage of nanoparticles. This demonstrates the recently expanding endeavors in utilizing environmental nanotechnology in diverse ecological areas (Patil et al. 2016). Because of the escalated urbanizing and man-made exploits, contamination has to turn out the main challenge for the environment. Therefore, the environment will not experience the bad effects of newer contaminants resulted from various advanced technicalities, yet additionally, the capacity of the environment to self-remediate would be diminished (Mehndiratta et al. 2013). In this manner, a pressing requirement is expected to trace the appropriate resolutions to lessen these contaminant level. Subsequently, nanotechnology is not just viewed as an emanating resolution to clean environment yet additionally for fighting contamination by mitigating pollutant formations and/or diminishing its emission (Mehndiratta et al. 2013).

As opposed to, remediation could be characterized as the study of decrease or evacuation of pollutants from soil, air, sediments, and water environments utilizing biological, chemical, and physical strategies. This remediation could be accomplished utilizing nanomaterials or nanoparticles. Those nanoparticles are having a few advantages attributable to their smaller size and higher surface region. Those nanomaterials/nanoparticles are having an incredible variety in their kinds which could be utilized for remediation purposes, inclusive of metal oxides, nanoscale zeolites, carbon nanotubes, dendrimers, enzymes, and bimetallic particles (Mehndiratta et al. 2013). Accordingly, nanotechnology is offering a modern generation of nanomaterials for remediating the environment. Remediation by this process has cost-efficient resolutions to challenge the issues of cleaning up the environment from contaminants (El-Temsah et al. 2016). For instance, few nanoparticles could be utilized for remediating soil or waste or ground water pollutions, because those nanomaterials are having the characterizations as follows: (1) extremely smaller sized nanoparticles could easily be injected into very smaller spaces that stay activated for a longer period, (2) larger surface areas could support in higher enzymatic activities, (3) the movements of those nanoparticles could be translocated along with the water flows by gravitational sedimentation process, and (4) those nanoparticles could be absorbed over the solid matrixes (Zhao et al. 2016; Louie et al. 2016; Araújo et al. 2015).

Remediation strategies could be categorized into biological, physical, and chemical techniques. Regarding the engineering and physico-chemical strategies, they are extravagant mentioning the uncovering of contaminated and waste disposals to a landfill in soils, prompting contamination somewhere else along with the handling and transportation of hazarding elements in the environments (Araújo et al. 2015). With respect to bioremediating methods, it is associated with the expulsion of hazarding contaminants utilizing plants (entitled phytoremediation), animals (entitled zooremediation), and microbes (entitled microbial remediation). As to zooremediation, it could be alluded to as a process for the expulsion of contaminants from hydrophyte ecological systems. Because of the moral and additionally human hygiene concern, the animals are very occasionally deliberated for bioremediation activities. Numerous investigations have already been published describing the appropriate nanotechnological resolutions to control contamination.

Plants as well as the microbes associated with them are utilized in tidying up various contaminations from water and soils, which is a promising technique termed phytoremediation (Ma et al. 2016). A few scientists have discussed phytoremediation which inclusive of phytovolatilization, phytostabilization, phytoextraction, phytofiltration, and so on (Wan et al. 2016; Shah et al. 2016; Mitton et al. 2016). It is likewise revealed that polluted environments have been phytoremediated utilizing nanoparticles (for example, nano-Au, CuO, ZnO, Ag, and C_{60}) which assimilate and translocate through plants as their nano or ionic forms (Patil et al. 2016; Singh et al. 2016). Regarding the microbial remediation process, it is forthwith announced that an advanced technique was introduced, where genetical engineered microbes are utilized to detoxify and degrade various contaminants in environment (Chandra 2015). Consequently, doubtlessly, the toxic elements

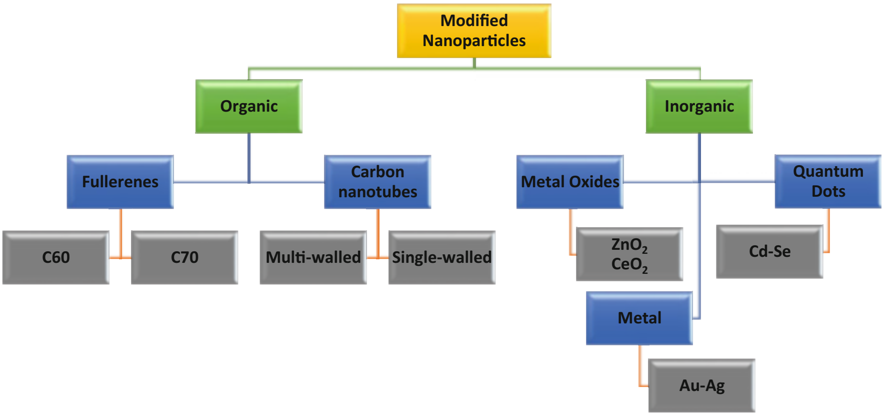

Fig. 1 Classifying nanomaterial as per their chemical–physical characters

released from continual anthropogenic operations are a major issue these days across the globe as it decays naturalistic resources like water, soil, and air. Presently, the great challenge is how all the nations could retain a sustainable environment. The control over pollutions could be attained via utilizing nanotechnology; however, additional control is required with numerous guidelines depending upon the nature and size of nanoparticles utilized (Sharma 2019) (Fig. 1).

6 Crop Propagation and Nanoremediation in Polluted Terrains

Nanoremediation is the usage of nanomaterials or nanoparticles for remediation or tidies up to the environment (ground and waste water, soil, sediment, and air) (Patil et al. 2016; Hamza et al. 2016). For instance, nanoremediation has few strategies in waste water treatment which includes nanomembrane filtering, photocatalysis, and absorption (Hamza et al. 2016). Nanoremediating by nanomaterials is probably the utmost potent technique for improving sustainable crop propagation in contaminated terrains. These strategies include the utilization of (1) agri-biotechnology, (2) nanobiotechnology, (3) root-biology, and (4) molecular biology that could be utilized for sustaining crop propagations in such grounds (El-Ramady et al. 2017).

The main threat and utmost significant concernment are related to the cultivation of consumable crops in contaminated terrains and their relation to the food cycle. Subsequently, it ought to be restrained potent risk factors for human hygiene, resulting from biomagnifying the contaminants by plants into the food cycle (Abhilash et al. 2016). To produce edible plants in polluted terrains which would be secure except having any harm to human hygiene, a few methodologies could be adopted that includes: (1) begetting by selecting fewer collector cultivars for those contaminants, (2) lessening bioavailability of those contaminants in soils, and

Table 2 Applications of nanoparticles in remediating soil and air

Nanoparticles	Target pollutants	Effects	Reference
Nanoparticles for remediating the soil			
Fe/Ni bi-metallic	Decabromodiphenyl ether (BDE209)	BDE209 present in soil can be degraded by Ni/Fe bimetallic nanoparticles at an ambient temperature, with a removing efficacy of up to 72%	Xie et al. (2014)
Nano zero-valent iron (nZVI)	Organo-chlorine insecticides (DDT)	1 gram nanoscale zero-valent iron (nZVI) per kg is effective for degrading DDT in spike soil, whereas a higher concentration utilized to treat aged pollutants present in soil	El-Temsah and Joner (2013)
Nano-crystal-line Hydroxyl-apatite (nHA)	Lead and cadmium	nHA effectively formulate Pb/Cd phosphate (hydroxypyromorphite-alike minerals) which lessen water-solubility, bioaccessibility, and phyto-available Pb/Cd	
Nanoparticle for remediating the air			
Silica nanoparticles (SiNPs)	Environmental lead (Pb)	The expanded adoption of Pb via SiNPs exhibited through the larger surfaces and the negatively charged groups within the SiNPs	Yang et al. (2013)
$Zn_{12}O_{12}$ nanocages	Carbon disulfide (CS_2)	At the adsorption energy of CS_2 per molecule decreased as the number of CS_2 molecules increased, which might be because of steric repulsion within the CS_2 atoms	Ghenaatian et al. (2013)
Aligned carbon nanotube	Aerosols	When the number of carbon nanotube layers increased and/or the pressure decreased, the filtration efficacy increased adequately	Yildiz and Bradford (2013)

(3) limiting contaminants take-up and their movement to those consumable portions (Abhilash et al. 2016). It is important to describe that the advantages of revitalizing contaminated terrains, incorporate soil carbon sequestration, safe phytoproducts, phytoremediation, and biofortification (Table 2).

As a new technique, nanoremediation strategies by utilizing nanomaterials eliminate pollution from the soil. Nanomaterials are having distinctive characteristics which could be implemented in various manners in remediating the soil. The utilization of nanoremediation techniques has benefits in comparison with conventional remediation techniques, which might be because of more specifically surface areas and modest particle size of nanomaterials and easy to move within the soil permeable. Likewise, this could be used for in situ application. Also, this strategy is more practical as well as economical for remediation, since it does not travel a long way from the targeted point (Tratnyek and Johnson 2006). Numerous distinctive nanomaterials have been proposed for remediating soil, for example, titanium

Table 3 Nanoparticles treating some polluted substances

Material class	Example of polluting substances
Organics chlorinated diluent	Chlorophenols, organophosphorus compounds, chlorinated pesticide
Inorganics anions	Nitrate, perchlorate, bromated
Metals chrome	Chrome, lead, cobalt, copper, nickel, molybdenum, silver, technetium, zinc, cadmium, vanadium

dioxide, metal oxides, nanoscale zeolites, carbon fibers and nanotubes, zerovalent iron, etc.

In addition, nZVI is presently more utilized for remediating contaminated soil. Table 3 displays a few instances of nanoparticulate materials applied in cleaning up of polluted soil (Thome et al. 2015).

Nanoscale nZVI These are quite possibly the most general kinds of nanoremediating methods that ranges from 10 to 100 nm in diameters. For the most part, the nZVI is distributed and transported within soil pores once infused for remediation of contamination (Tratnyek and Johnson 2006). Due to their properties (like higher surface areas, higher reactions, and higher efficacy), they could be utilized in in situ remediating technique (Henn and Waddill 2006).

Mechanisms of nZVI in Decontamination Nanoremediating techniques utilizing nanoparticles (NPs) for remediating could be classified into two sections relying upon their chemical reactions: the first section utilized NPs as the electron donors for removing the contaminations to a lower extent of toxic with slower transportation into the soil and the second section utilized NPs as a sorbent agent which is more static for toxic obsession; in addition, it could be utilized the NPs as co-precipitant or precipitant of the contaminated elements. Specifically, NPs are having a higher adsorption ratio for metals (anionic contaminants), like lead (Pb), copper (Cu), chromium (Cr), uranium (U), arsenic (As), selenium (Se), mercury (Hg), heavy metals, organic acids, and natural organic matters (Thome et al. 2015). The reactions in between NPs in nZVI technique with toxic materials depend on the higher surface areas of the substances and basically that this substance could be sequestrating toxic or contaminated substances in two different ways first and foremost by encapsulating toxic substances in the interfaces of NP aggregate, and second by complexation surface fixation (Thome et al. 2015). In general, the chemical reactions that occurred in zero-valent iron (Fe^0) nanoparticles for removing heavy metals and organic halogenated pollutants from soil could be explained by the subsequent equations:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^0 \rightarrow Fe^{3+} + 3e^- \quad (2)$$

$$RCl + 2e^- + H^+ \rightarrow RH + Cl^- \quad (3)$$

$$RCl + Fe^0 + H^+ \rightarrow RH + Fe^{2+} + Cl^- \quad (4)$$

As appearing in the above reaction, the Fe^0 transformed into Fe^{2+} ion (Eq. (1)) by donating electron (first way of clean up), additionally, might progressively be by more period to Fe^{3+} (Eq. (2)). While the reduction reaction between chlorohydrocarbons and electrons is utilized in Eq. (3) to dechlorinate the soil. Moreover, the coupling of the reactions Eqs. (1) and (3) as shown in Eq. (4) could be suitable by thermodynamic processes. Below are the chemical mechanisms of nanozerovalent iron (Fe^0).

In general, the standard reduction potential (E°) of the Fe^0 to convert to Fe^{2+}/Fe ion is –0.44 mV, demonstrating that the higher capability of Fe^0 ion reduces contaminations of numerous organic compounds like chlorinated hydrocarbons and metals (Cd, Cr, Ni, and Pb). Degrading organic pollutants by Fe^0 technique has two general processes: (1) hydrogenolysis in chlorinated components, where the Cl atom is substituted by H atom, as shown in Eq. (5), and (2) dehalogenation, in which no amalgamation of H, but a newer carbon–carbon bond could be constructed and it could be divided into two types of reactions based on the carbon attached: α reaction (might be associated with same carbon) and β reaction (associated with neighboring carbon). The below reactions are shown in Eqs. (6) and (7), respectively (Sharma 2019):

$$CHCl = CCl_2 + 2e^- + H^+ \rightarrow CHCl = CHCl + Cl \quad (5)$$

$$\text{Reaction } \alpha : CCl_2 = CH_2 + 2e^- \rightarrow H_2C = C : +2Cl \quad (6)$$

$$\text{Reaction } \beta : CHCl = CCl_2 + 2e^- \rightarrow HC \equiv CCl + 2Cl \quad (7)$$

In s soil by the Fe^0 method, it is preferable to utilize dehalogenation reaction than hydrogenolysis process, because as a result of hydrogenolysis reactions, a new substance which is more harmful compared to the contaminant resource might be formed (Sharma 2019). Thus, nanotechnology provides the probability of formulating higher quality and lower cost nanomaterial products for remediating the soil compared to conventional procedures. Nanoremediation techniques involve the utilization of nanoparticles to absorb, detoxify, and discharge pollutants from the soil in situ remediation method. Furthermore, the nZVI techniques could be utilized for the demolition of chlorohydrocarbons in the soil.

In general, nZVI could be infused within a place for degrading the contaminants by making a parapet of particles that tidy up the water by passing through it or by utilizing mobile particles, i.e., adequately smaller to pass via the soil pores (Fig. 2) because of their higher surface area contrasted with bigger iron particles, leading to faster reaction rates. Therefore, nZVI is an alluring alternative for in situ remediations.

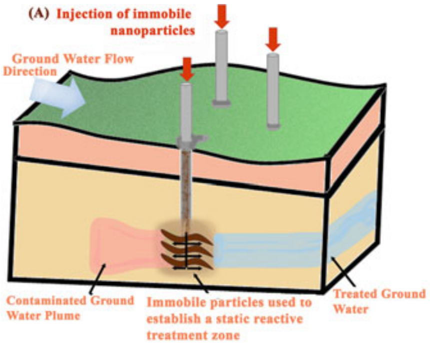

Fig. 2 Schematic representation of how the (**a**) immobile nanoparticles and (**b**) mobile nanoparticles are infused into the sub-surface for groundwater treatment (Reproduced from Crane and Scott 2012, with permission)

7 Drawbacks and Risks of Nanoparticles

The utilization of nanoparticles is a quickly arising strategy with a huge numeral of advantages. It has been shown in studies to be an extremely quick and effective process for remediating polluted soil, ground water, and surface water (Thatai et al. 2014; Wang et al. 2014). There are also some disadvantages and risks associated with the utilization of nanoparticles, for example,

1. Absence of proper or complete behavior and knowledge about nano-nZVI nanoparticles in the environment and their potential ecological consequences.
2. nZVI in higher concentrations could agglomerate to formulate clusters, thus results in loss of activities as a nanoparticle.
3. The smaller size and higher mobility of nanoparticles could easily be dispersed into the environment and subsequently might be distributed over larger distances resulting in ecotoxicity. Nanoparticles are likewise profoundly persistent and pose a risk of bioaccumulation living beings (Grieger et al. 2010).
4. Some nanoparticles, such as nZVI, have wider side effects on living organisms. nZVI can be oxidized by such bacterial cultures, such as sulphate-reducing bacteria. However, the oxidizing higher concentration level of nZVI leads to form reactive oxygen species (ROS) (Sharma 2019). Accumulation of ROS might result in oxidative stress, which could damage cell membranes and eventually lead to death.
5. According to reports, nZVI in higher concentrations shows a stronger toxic impact in plants, subsequently decreasing the transpiration rate as well as translocation to the shoots (Ma et al. 2013). Plants with reduced transpiration and translocation will experience stunted growth and eventually die if exposed for an extended period. In humans, nanoparticle exposure has been linked to genotoxicity, lipid peroxidation, inflammation, oxidative stress, and pulmonary disease, all of which may lead to death (Sharma 2019).

8 Solutions to Drawback of Nanoremediation

The procedure of nanoremediation even though being exceptionally rapid and effective has various disadvantages and ecological risks related as mentioned earlier. The issues can be settled by providing better solutions for effective management:

1. Green nanoparticles made from plants and plant parts are utilized to reduce the release of harmful by-products into the environment, thus lowering ecological toxicity.
2. Likewise, implementing nanoparticles derived from microbes also termed bionanoparticles, for biodegrading heavy metals in acid mine water could be a snappy and effective strategy. Fungi also called "Nanofactories" are highly appropriate for synthesizing metal nanoparticles (Dhillon et al. 2012).
3. The drawbacks associated with Fe^0 could be solved by utilizing emulsified zero valent iron (eZVI) which is formulated of iron nanoparticles encapsulated in a biodegradable oil membrane. The surface coating protects the nZVI from other constituents or inorganic contaminants that could interfere with the iron and reduce its capability (Sharma 2019).

Plant activities should be well-researched before being selected for the remediation phase as a solution to the problems, and their efficacy ought to be verified. The combination of ideal plants, appropriate soil amendments, and rhizospheric microorganisms could be proven as an efficient remedial strategy. The utilization of plants in the remediation strategy could be prevented by enclosing the phytoremediation area in a fence.

9 Conclusions

It may be inferred that the usage of nanotechnology for toxin remediation has acquired promising outcomes. Besides, utilizing nanomaterials/nanoparticles as a catalyst or/and sensing systems, nanoremediation might provide a pathway to purify the air, water, and soil resources. Remediating the groundwater to drink as well as reutilize is a promising area that could be accomplished by utilizing nanomaterials like Fe^0 and carbon nanotubes. Nonetheless, there are still several unresolved inquiries about the possible dangers and human hygiene implications of using nanomaterials in the environments. Many economic, social, and ecotoxicological considerations, as well as a few procedures for limiting the possible dangers for human hygiene, ought to be remembered when it comes to sustaining crop production from contaminated terrains utilizing nanoremediation. Besides, restoring soil usefulness and monitoring plants development in contaminated terrains are vital before any field recommendations for utilization of nanoremediation.

Therefore, nanoremediation could be considered as an interesting approach with regard to managing both environmental health as well as safety terms, while there is not completely understand regarding the behavior of nanomaterials/nanoparticles over a larger scale. In this way, the utilization of nanomaterials/nanoparticles for remediation ought to be trailed by additional protection and adequate investigations. Moreover, the contaminated terrains address a tangible threat to the environment especially in the case of hazardous pollutants, yet then again, those contaminated soils might also provide a true benefit for the multi-cropping in food production and biorefineries for the bio-economy. Furthermore, investigations are required in managing nanoremediation, which include (1) the biotoxication of nanoparticles/ nanomaterials (for example, the portability and biogeochemistry of those nanoparticles specifically underneath the field factors), (2) the examination of local environmental factors and their impacts on nanomaterials/nanoparticle transportation and transformations, and (3) investigate the synergistic as well as antagonistic benefits of nanoparticulates and microbial actions in soil.

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Nanoremediation of Heavy Metals in Agricultural Soil

Aryadeep Roychoudhury and Rituparna Bhowmik

1 Introduction

Ever since its emergence in 1980, nanoremediation turned out to be a powerful technique for controlling pollutants ranging from 1 to 100 nm (Mansoori and Soelaiman 2005). The branch of environmental nanotechnology deals with innovative and effective strategies of remediation using nanoparticles (Bayda et al. 2019). Several anthropogenic activities reduce the self-remediation ability of environment, while nanotechnology-based approaches emerge as effective solutions for cleaning the environment of its pollutants. While the organic pollutants may be easily degraded into harmless products, inorganic heavy metal contaminants like arsenic, lead, chromium, cobalt, etc., are recalcitrant to natural degradative processes. These heavy metals tend to persist in soil, and are particularly difficult to remove, immobilize, or reduce completely (Fulekar et al. 2009). Remediation, by definition, is the process of reducing pollutants in soil, air, water, and sediments by means of physical, chemical, or biological means. This chapter will specially focus on remediation of heavy metal-contaminated soil by means of nanoparticles. Thus, the obvious question arises—why nanoparticles? Nanoparticles are exceptionally good for remediation owing to their high surface area and small size. In addition, nanoparticles are available in a wide variety of types like carbon nanotubes, dendrimers, bimetallic particles, enzymes, nanoscale zeolites, zero-valent iron, and in the form of metal oxides (Mehndiratta et al. 2013). Of all these techniques, zero-valent iron appears to be one of the simplest and most cost-efficient, with immense applications like adsorption, catalysis, and reduction of heavy metals for

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remediation. This chapter will deal with some of these new nanotechnology-based remediation processes and the scope of their application in practical scenarios.

2 Heavy Metals and the Hazards They Pose

Contaminants of the environment may be in the form of organic exudates, bacterial or viral particles, dyes, or heavy metals like lead, cadmium, zinc, arsenic, nickel, chromium, and mercury which are non-biodegradable in nature and pose a serious risk to human health. In recent times, the problem of soil trace elements has reached a menacing level, with about 40,000 km^2 of soil in Europe reported to be polluted by heavy metals (El-Ramady et al. 2017). Such heavy metal pollutants can have far-reaching consequences pertaining to specific behavior of that element, or general effects that most trace heavy metals display. For instance, heavy metals have the tendency to bind with organic molecules like proteins and nucleic acids, thus interfering with metabolic processes and leading to mutations which may even lead to adverse conditions like cancer (Sardans et al. 2011). Agency for Toxic Substances and Disease Registry (ATSDR) enlisted a series of contaminants that pose a threat to living organism based on their frequency of occurrence, toxicity, and possibility of human exposure. The list includes heavy metal contaminants as follows (Xue et al. 2018).

Rank	Heavy metal	Total points
1	Arsenic	1676
2	Lead	1531
3	Mercury	1458
7	Cadmium	1318
17	Hexavalent chromium	1143
52	Cobalt	1011
58	Nickel	993
66	Chromium (VI) trioxide	961

Studies confirm that 52,000–112,000 tons of toxic metalloid like arsenic is released annually into the environment due to industrial activities (Nriagu and Pacyna 1988; Huang et al. 2018). Arsenic stands as a priority hazardous pollutant in lieu of its extreme toxicity to humans, animals, and plants, even in trace amounts. Graphene oxide (GO) nanoparticles may be used for remediation of such arsenic-contaminated soil (Baragaño et al. 2020). Lead is another potent heavy metal pollutant from mining sites, manufacturers of acid batteries, paper, glass, and polishing industries. The Center for Disease Control and Prevention (CDC) 1992 reported that paint is the major contributor of lead contamination in soil [Binder S and Matte T (1992) Review of soil lead levels, personal communication]. Children suffering from elevated levels of lead are found to have lower dietary intake of calcium and phosphorous. Some studies also indicate zinc deficiency, resulting from enhanced lead absorption (ATSDR 1988, 1992). Lead toxicity may occur with soil levels of lead higher than 10–15 μg/dL causing neurobehavioral effects and motor skill deficits (CDC report 1992). Cadmium is another potential hazard to human health that increases the risk of bladder, breast, and lung cancer. Nanoscale zero-valent iron (nZVI) has the potentiality to remediate cadmium contamination (Xue et al. 2018). Nickel contamination can lead to skin problems when they come in contact with jewellery trashing, watches, zippers, etc. Discarded batteries, photovoltaic cells, metallurgical industries, fabric factories, etc. are the sources of chromium contamination (Moreno Castilla et al. 2004). There are reports of congenital malformation of body parts, and even cancer from occupational chromium exposure in mining sites (Van et al. 2020). Cr(VI) is a potent respiratory carcinogen that leads up to 100,000 deaths globally. Respiratory carcinogens impacted 0.1 million death globally (WHO 2016). Manganese is a heavy metal which finds extensive use in electronics, battery manufacture, metallurgy, and chemical industry. Manganese and its multiple oxidative states (like Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{6+}, and Mn^{7+}) are potent heavy metal pollutants usually found in mining areas such as Xiangtan city of Hunan, China. These are known to cause several problems in human central nervous system and endocrine system (Baby Shaikh et al. 2018). Such detrimental effects of heavy metal poisoning necessitate remediation methods via nanotechnological means. In this chapter, we will discuss a few such methods in detail.

3 Nanoremediation of Ground Water, Wastewater, and Soil

Nanoremediation is an eco-friendly, often cost-effective method of cleaning up heavy metal-contaminated sites. This often involves the addition of reactive materials, which detoxifies the contaminated region by transformation of the pollutants into harmless states, or by immobilization. The unique properties of high reactivity, small size, and large surface area allow nanoparticles to effectively clean up better than the larger sized particles (Karn et al. 2009). Nanomaterials like nanomotors, nanomembranes and nanosorbents may be used for effective treatments of contaminated ground water and wastewater. Nanophotocatalysis makes use of UV-light/visible light/sunlight for activation or stimulation of nanomaterial for effective decontamination of heavy metals. Microporous nanomembranes may also be used to eliminate unwanted minute contaminants from aqueous phase. Often, this is used as a pre-treatment process with reverse osmosis (Jhaveri and Murthy 2016). The carbon polymer-based membranes like carbon nanotubes and graphene oxide membranes may in turn be doped with nanomaterials like zeolites, alumina, or titanium oxide (Waduge et al. 2015). Several nano- or micro-motors are now being tested for water remediation, which includes

- Platinum-coated activated carbon-based motors for targeting heavy metals like lead, dyes, or nitroaromatic explosives (Li et al. 2011).

- DNA functionalized gold/platinum microtubes for mercury remediation (Wang et al. 2016).
- Graphene oxide with nickel or platinum for lead remediation, etc. (Zhang et al. 2019).

Nanoparticles may be carbon-based materials like carbon nanotubes, or non-carbon-based materials, such as zero-valent iron. Of these, zero-valent nanoparticles are now widely used in groundwater remediation, contributing to considerable reduction in non-aqueous phase liquids. With this success, nanoparticles are becoming the go to option for in situ clean-up of underground oil spills. Industrial and medical wastes also contaminate soil with toxic levels of heavy metals which pose a serious problem to humans, animals, and plants. Nanomaterials such as GO and zero-valent metals are very effective against such heavy metal pollutants. These techniques would be discussed in the underlying sections.

4 Soil Nanoremediation

With rising population, crop production needs to be sufficient to feed the world population. There must be sufficient production of crops for human consumption (food crops) as well as for other purposes like horticulture, biofuel biomass, etc. One way to increase productivity could be by utilizing the polluted lands, which amounts to a staggering one-third of arable lands. Remediation of this large area could solve the space crunch for sufficient productivity in today's world. Inventions like nanomaterials that can remediate heavy metal contamination would thus have large impacts in agro-biotechnological sector, ensuring food safety and sustainability (El-Ramady et al. 2017).

Some basic factors need to be considered for sustainable crop production:

- The income, possible from the polluted land.
- The number of contaminating metals.
- The overall safety of the process and use of products grown on polluted land.
- The manner in which crop behavior is affected by polluted land.

While heavy metal polluted land poses serious threat to human health, nanoremediation could be a suitable solution to meet the demands for arable lands for agriculture (Abhilash et al. 2016).

5 Use of Carbon Nanoparticles in Heavy Metal Remediation

Techniques to immobilize, degrade, and destroy soil heavy metal contaminants can be divided into in situ and ex situ techniques. While in situ techniques are employed at the actual site, ex situ techniques may include excavation, remediation, etc. Soil contaminants like heavy metals are not degradable like organic wastes; hence, stabilization or solidification is generally applied in situ to remediate heavy metal-contaminated soil. These techniques minimize the rate of mobility of the contaminant in soil, thus reducing exposure to living beings. Such immobilization techniques are attempted via three mechanisms: (1) the contaminants are fixed by means of chemical bonds between binding chemicals and the contaminant; (2) absorption of the contaminant on the surface of the binder; and (3) physically trapping the heavy metal waste by encapsulation. For remediation of metals like chromium, nickel, etc. from contaminated soils, the following types of carbon nanoparticles may be used:

- Carbon nanotubes (CNTs)
- Graphene oxides (GOs)
- Reduced carbon dots (CDs)

5.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are devised from allotrope of elemental carbon, which may be used for remediation by the second CNTs, to 100 nm wide multiple-walled CNTs interlinked together. CNTs are bound by sp^2 bonding which confers upon them strong binding capacity needed for different applications like remediation that requires large surface area and adsorption quality. Often, CNTs are functionalized with reducing agents and some catalysts that convert Cr(VI) (potent respiratory carcinogen) to less harmful Cr(III) (Zhu et al. 2019). Carbon nanotubes with single walls are found to be less toxic compared to double-walled counterpart (Jones et al. 2019). Ever since its first application in 1991 by Sumio Iijima, unique property of CNT has gathered sufficient interest among the scientific community. CNTs fall into two groups:

- SWCNTs: single-walled carbon nanotubes—which as their name suggest are composed of single graphene tubes (Fig. 1).
- MWCHTs: multi-walled carbon nanotubes with multi-layered graphene tubes (Fig. 1).

With their high surface area and absorption properties, CNTs can attract and retain large amounts of heavy metals on their surface, thus becoming a suitable candidate for remediating heavy metal-contaminated soil (Renew et al. 2016; Gupta and

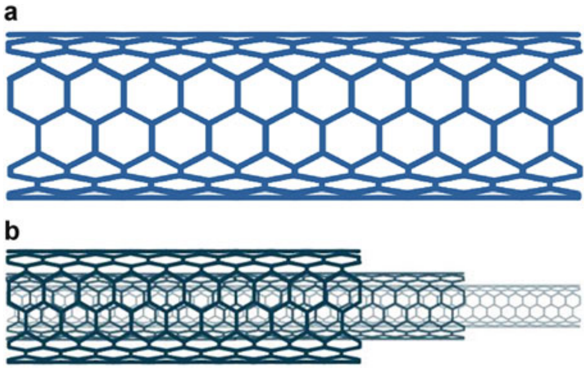

Fig. 1 (**a**) Single-walled carbon nanotube. (**b**) Multi-walled carbon nanotube

Surwade 2007). Satisfactory results have been observed from CNT application in heavy metal-contaminated soil and water. In case of copper (Cu^+) contamination, only a small amount of CNTs could remove about 96% of copper from contaminated soil. Studies also showed that MWCNTs could possibly remediate cadmium, lead, and zinc along with copper. While the absorption capacity of MWCNT is different for different heavy metals, reports show approximately 99% removal of lead and copper. With such high efficiency, CNTs find immense application in immobilizing heavy metals in contaminated soils (Kabbashi et al. 2009; Abdel Salam 2013).

5.1.1 Technical Challenges of Using CNTs for Heavy Metal Remediation

For expressing high absorption quality, prior treatment of CNT is necessary. One more parameter that may hinder the widespread use of CNTs is its tendency for agglomeration. The highly specific surfaces of CNTs are involved in Van der Waal's force of attraction between surfaces, and this may form clogs that would in turn reduce absorption capacity for soil contaminants. Ways to avoid agglomeration include use of mechanical or chemical techniques such as ultrasonic waves, covalent, and non-covalent changes on the surface and surfactants. The ultimate mechanical method applied to clear agglomeration is ultrasonic energy. There needs to be a critical balance between the energy and duration of the ultrasonic wave application, to prevent damage to the CNTs. Chemical modification and surfactants tend to adsorb on the CNT surface, thus changing its surface property and outer structure. Such chemical techniques could also help to dispense the CNTs by changing their steric or electrostatic interactions. A blend of both the techniques can be used for maintaining the long-term efficiency of CNTs (Rossell 2013).

Another important determinant of the CNT efficiency is the contaminated soil itself. Soil properties like pH, organic content, and amount of silt, sand, and clay particles have altogether a huge impact on the nanotube efficiency of remediating heavy metals from soil. Fine-grained soil with substantial quantities of silt and clay is good for retention of heavy metals, while the heavy metals become more mobile and harder to restrict in acidic soils (Kumpiene et al. 2008). The organic content of soil may be involved in physical and chemical interactions with heavy metals like lead and copper and reduces mobility of soil contaminants (Gomes and Fontes 2001). However, organic contents show poor affinity for metals like zinc and copper. On the other hand, excessive water infiltration in course-grained soil may wash away the heavy metals, leading to further spread (Houben et al. 2012).

The properties of CNTs and MWCNTs for use as soil remediating agents have been compared by Matos et al. (2017). They used several mechanical and chemical methods to dispense the carbon nanotubes and prevent agglomeration. They also used Pluronic F-127, a non-ionic surfactant. They tested samples of artificially contaminated soil treated with CNTs and MWCNTs for several parameters like permeability, surface adsorption of individual nanotubes as a whole, and competitive adsorption in case of more than one heavy meal contaminants. This study revealed that different heavy metals are bound to soil with different affinities. Lead is the most strongly interacting metal with soil in the presence of no additive, while zinc showed the least affinity; copper and nickel have intermediate affinities, with copper binding somewhat stronger than nickel. Adsorption tests revealed that lead and copper were only slightly affected by introduction of nanotubes in soil, since they were already strongly adsorbed to soil particles. MWCNT application improved the immobility of zinc and nickel in soil by 30%. Even permeability tests of the soil confirmed that MWCNTs improve soil retention of nickel and zinc with almost complete immobilization, leading to remediation of the contaminated soil. Thus, MWCNTs can be suitably used for stabilization or solidification techniques for soil, for remediation of metal-contaminated soil.

5.2 Graphene Oxide (GO)

Graphene oxide (GO), made from chemical exfoliation of graphite, is an extremely oxidative form of graphene (Ku and Park 2013). As a recent chemical discovery, graphene oxide appears to have some very interesting features (Bai et al. 2017; Chung et al. 2015; Kim et al. 2010; Stankovich et al. 2006) like:

- High reactivity
- Enormous surface area

GO, is a single layer of 2-D graphite sheets with a number of oxygen containing functional groups like OH (hydroxyl), epoxy, and –COOH (carboxyl), which induce strong electrostatic interactions with hexavalent chromium in heavy metal-contaminated soil. The carbonyl oxygen groups have lone pairs that form efficient *p–p* bonds, with the Cr(VI) existing in contaminating chromate forms. In addition, these oxygen molecules also allow GO to form hydrogen bonds with water, allowing water solubility. This property helps in removing pollutants from soil in solution phase (Neklyudov et al. 2017).

The GO monolayer is 1 nm in thickness, but it may extend in order of micrometers in length and width, leading to large surface area for efficient heavy metal ion adsorption. While the GO sheets use similar strategy as CNTs by using functional groups that can interact with hexavalent chromium, quite unlike CNTs, these groups are mainly made up of polyethylenimine, coated with positively charged groups which accelerate adsorption kinetics (Wang et al. 2017). When experimentally tested, GO showed notable effect on increasing As metal availability in soil. It suitably immobilized lead, cadmium, and zinc (Baragaño et al. 2020). While lead and copper immobilization significantly increased as the dose of GO was raised, Cd availability was only slightly affected by increase in GO concentration. In contrast, significant zinc immobilization was only reported at high concentrations of GO.

The acidic and basic nature of GO based on the nature of its components may affect the soil pH and electrical conductivity. In usual case, soil pH decreased with use of GO in increased concentrations. GO is also known to increase electrical conductivity of soil, but even at the highest doses, it is lower than 2 dS $^{m-1}$ which could not lead to any salinity problem. Application of GO in arsenic-contaminated soil may also tend to reduce soil phosphorous availability, due to competition (Baragaño et al. 2020). The increase in soil arsenic mobility in response to GO application is possibly due to the large number of carbonyl groups that present a negative charged surface to the GO. This capacity of GO to increase As mobility may be put to use to enhance phytoextraction strategies by plants like *Pteris vittata, Brassica juncea, Helianthus annuus,* or *Zea mays* (Mandal et al. 2018; Franchi et al. 2019).

5.3 Carbon Dots

Carbon nanodrops (Fig. 2) are a new type of nanomaterials that were accidentally discovered during purification process of SWCNTs (Xu et al. 2004). CDs, also known as zero-dimensional fluorescent carbon molecules, are well-known for their biological compatibility, cost efficient preparation, and least harm to nature. These water-soluble CDs (wsCNDs) are non-toxic to crop plants and may be used to remediate heavy metals like cadmium from agricultural fields. Ranging from 1 to 10 nm, CDs help in heavy metal remediation by means of photocatalysis. They are tunable by doping with N and P leading to reduction of harmful Cr(VI) in soil to Cr (III) through photocatalysis (Bhati et al. 2019). CDs can be doped with nitrogen by thermolysis method in which the starting materials are heated at 280 °C for 100 h by photocatalysis. CDs are also known to alleviate cadmium-mediated abiotic stress in plants, by virtue of their property of heavy metal adsorption. These CDs are biocompatible and non-toxic. Incubation with 0.4 mg/mL of CDs was shown to promote growth of plants like mung bean. They were also known to be transported from root to shoot in mung beans (Xiao et al. 2019).

Carbon nanodrops may be synthesized by two approaches:

Fig. 2 Carbon dot

- Top-down approach which includes use of laser ablation, arc discharge, microplasma treatment as well as electrochemical techniques (Biazar et al. 2018; Ma et al. 2019; Shadjou et al. 2016).
- Bottom-up approach which includes methods like pyrolysis, polymer carbonization, use of microwave and reverse micelle method (Pajewska-Szmyt et al. 2020; Prikhozhdenko et al. 2018).

Another suitable method of CD production was discovered by autoclaving titanium oxide nanoparticles with CDs together in a Teflon autoclave at 150 °C for 10 h. This hydrothermal method modified the titanium oxide nanoparticles with CDs on their surface, which could in turn be used for photocatalytic reduction of hexavalent chromium (Acharya et al. 2018).

The reduction mechanism of the CDs is as follows:

- When light falls on nanoparticles modified with CDs (NP–CD), positive charged regions and negative electrons are generated in the valence shell and conduction bands.
- These positive regions interact with water molecules, splitting it into oxygen and hydrogen molecules.
- The released electrons interact with heavy metals like hexavalent chromium, and together with the photons, they reduce Cr(VI) to Cr(III).

For effective reduction, slightly acidic pH is preferred which maintains the chromium ions in chromate (CrO_4^-) or dichromate (Cr_2O^{2-}) forms. Reduced trivalent chromium can be easily precipitated as hydroxides, by addition of strong alkali like NaOH. One complication during this process may arise from the positive holes and negative electrons interacting together and nullifying each other. To prevent this, NP–CDs could be doped with inorganic particles like titanium oxide nanoparticles which introduce a spatial separation of charges in photocatalytic reactions.

The mechanism may be depicted by the following equations:

$$\text{Titanium oxide doped NP–CD} + h\nu \rightarrow h + e^- .$$

Here, $h\nu$ is the incident energy in photons, which generated the positive holes h^+ and mobile electrons e^-. The tetravalent titanium traps the photogenerated electrons, preventing them from nullifying by recombination with the positive holes:

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ .$$

The h^+ generated from the positive hole splits water molecules into oxygen and releases photons. Oxygen interaction with tetravalent titanium releases trapped electrons. In acidic medium, chromates enter an equilibrium state with dichromate, which are reduced by the photons and electrons to form non-toxic Cr(III):

$$2HCrO_4 \leftrightarrow Cr_2O_7^{2-} + 2H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O.$$

This efficiency of reduction is improved in N- and P-doped CDs, and in case of finer sized CDs with lager surface areas. Interfering ions like chlorides, sulfates, nitrates, etc. show little effect on reducing potential of these CDs (Bhati et al. 2019).

6 Non-carbon Nanomaterials

Two well-known alternatives to carbon-based nanomaterials are:

- Zeolites
- Zero-valent iron nanoparticles

6.1 Zeolites

Zeolites are naturally occurring microporous minerals. Nano-zeolites range from 10 to 100 nm in size, with ample electrostatic charges on the surface. These are made up of aluminosilicate crystals, with water or oxygen molecules bound to the charged surface. The finer these nanomaterials are, more the surface area they cover to physically entrap the heavy metal contaminant (El-Sayed 2020).

Nanozeolites may be synthesized by gradually dissolving silicon and aluminum-based minerals in strong alkaline medium at optimal physical conditions. The dissolved minerals would then nucleate and eventually form crystals of mesoporous nanozeolites (Mafra et al. 2012). Sometimes, a seed of zeolite may also be added to initiate crystal formation. Fused alumino silicate when dispersed homogeneously in deionized water and ultrasonicated, rapidly crystallizes to form nanozeolites at 80 °C. While their exact mode of action is unclear, zeolites are expected to adsorb heavy metals like Cr(VI) on their surface micropores from acidic medium. Yet, nanozeolites are rather expensive and suffer from the problems of hydrophobic film development. This often makes it inaccessible to the contaminating heavy metals, thus defeating the purpose (Antoniadis et al. 2018).

6.2 *Zero-Valent Iron Nanoremediation*

Another cutting-edge nanomaterial is the zerovalent form of iron nZVI. Iron is the most desired abundantly available catalytic transition metal, with many other forms like oxides; this makes it a perfect cost-effective material for nanoparticles. nZVI has a zero-valent iron at its core which is enclosed in a shell of oxide or hydroxides. This outer shell keeps growing thicker as the oxidation process proceeds. Like zeolites and carbon nanotubes, zero-valent iron also has a large surface area, high adsorption capacity, and high reactivity which makes it suitable for large scale nanoremediation. (Emadi et al. 2016; Tafazoli et al. 2017). The high reactivity of nZVI with excellent electron-donating potential may be attributed mainly to the large surface area and the inherent property of the particle surface. Reactive sites densely occur on nZVI surface making reaction pockets (Gil-Díaz et al. 2014).

nZVI are manufactured from iron ions using reducing agents which donate their hydroxyl group to the iron core. The zero valency and magnetic property, however, make this nanomaterial prone to agglomeration that halts further adsorption and reduction on that surface. This may be prevented by functionalizing the surface with various polymers by conjugation. nZVI are often synthesized while embedded in a supporting medium of carboxymethylcellulose-mediated sodium alginate beads. A combination of nanomaterials may also be used by doping nZVI on CNTs. Here, the reducing iron precursors could be coated on CNT surface by ultrasonication in aqueous medium. In addition, nZVI may also be conjugated with graphene nanosheets, or titanium oxide nanoparticles to enhance their remediation potential (Li et al. 2006; Petala et al. 2016). The precursor form of iron used for nZVI is $FeCl_3.6H_2O$. $NaBH_4$ is used to reduce $Fe^{3+} \rightarrow Fe^0$ in aqueous medium while conjugating it over other nanomaterials. The simple synthesis, ample raw material availability, and excellent adsorption capacity make nZVI economically feasible remediating agent.

The interaction of nZVI with heavy metal contaminants may be simplified as:

1. Reduction
2. Adsorption
3. Oxidation/reoxidation
4. Co-precipitation
5. Precipitation

Reduction occurs in aqueous medium through beta-elimination (Dong et al. 2019a):

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

The electrons that are ejected now interact with available water molecules and give off hydroxide molecules (Ken and Sinha 2020):

$$e^- + H_2O \rightarrow H^+ + OH^-.$$

This dissociated water molecule interacts with heavy metals like Cr(VI) in acidic medium, reducing it to hydroxide state (Brasili et al. 2020):

$$Fr^{2+} + Cr + 4H^+ \rightarrow Cr(OH)_3 + Fr(OH)_2 + 3OH^-.$$

Reduced non-toxic chromium hydroxide precipitates as a result of reduction. Smaller is the size of nZVI, more is its reduction efficiency and rate. With time, the zero-valent iron in core is gradually oxidized and the size increases as this oxidized iron forms a product layer around the nanomaterial. If the concentration of metal contaminant is very high, this product layer formation is slower. The presence of other ions like nitrates may also reduce the efficiency of nZVI (Vilardi et al. 2017). The heavy metal cations are also less remediated by nZVI in extremely acidic conditions, while anions are not properly reduced in alkaline conditions due to variation in proton transfer in such pH.

The different methods of synthesis of nanomaterials are summarized in the following table:

Material	Synthesis method	Reference
Graphene oxide nanoparticles	Modified Hummer's process with $KMnO_4$ or $K_2FeO_4^-$	Alam et al. (2017), Peng et al. (2015)
Carbon nanotubes	Hydrothermal method or pyrolysis with ultrasonication	Dong et al. (2019b), Zhu et al. (2019), Mohamed et al. (2016)
Carbon dots	Hydrothermal method	Li et al. (2018)
Zeolites	Seed induced hydrothermal or ultrasound assisted hydrothermal technique	Li et al. (2017), Sivalingam and Sen (2018)
nZVI	Chemical reduction of graphene oxide Ultrasonication with CNT Alginate encapsulation Coacervate with TiO_2 nanoparticles	Vilardi et al. (2018) Li et al. (2019) Petala et al. (2016)

7 Self-Toxicity of Nanomaterials

Some nanomaterials display a self-toxic tendency. Some metal oxides display toxic character even at low concentrations (Brandao et al. 2015). The toxicity of the nanomaterials depends on properties like:

- Length
- Distribution ratio
- Surface area
- Aggregation degree

Nanoparticles made of copper oxide (CuO) are now being tested for their fungicidal properties. However, accidental spills of CuO nanomaterial in soil could even be a potential cause of contamination. Plant roots release some exudates that improve the mobility and availability of minerals, such as metal chelators. These metal chelators may interact with CuO nanoparticles in rhizosphere added as fungicides and impact plant growth. Studies show that CuO nanoparticles interact with exudates like phytosiderophore and deoxymugineic acid (DMA) at high nanoparticle concentrations. When crops such as wheat are exposed to these nanoparticles in dose-dependent manner, the availability of other minerals like iron, calcium, magnesium, manganese, and potassium is reduced in roots and shoots at higher concentrations. There may also be sort of rhizopheric interactions between CuO nanoparticles and root exudates of plants like wheat growing in sand matrix, which affect the availability and uptake of nutrients by the plant (Rajput et al. 2019).

The toxic effects of titanium oxide nanoparticles depend on the initial concentration of nanomaterial. However, even higher concentrations are non-toxic with 24 h exposure. These nanoparticles may cause lung problems, oxidative stress, inflammation, apoptosis, and fibrosis. Further studies are needed to understand the process of degradation and elimination of these nanoparticles in our body for safer application (Hogen-Esch et al. 2019; Waduge et al. 2015).

8 Practical Applications of Above-Mentioned Nanoparticles So Far

Baragaño et al. (2020) tested the ability of graphene oxide nanomaterial against nZVI in remediation of arsenic-polluted soil. Their results showed that nZVI could effectively be used to reduce arsenic bioavailability in soil, while the final availability would depend on initial concentration and presence of other metal contaminants. However, arsenic bioavailability was rather increased in the presence of graphene oxide nanoparticles. Therefore, while immobilization of arsenic pollutants in the presence of nZVI could be one option for nanoremediation, phytoextraction or phyto-stabilization of arsenic in presence of GO could be another alternative. GO nanoremediation also helps to improve certain physio-chemical properties of soil like phosphate availability and opens an avenue for application of hybrid techniques for nanoremediation. GO could also possibly have a role in immobilizing Cu in soil (Baragaño et al. 2020).

Chromium (VI) contamination is associated with severe health risks including cancer. Azeez et al. (2021) extensively studied nanoremediation of Cr(VI) by various carbon-based and non-carbon-based approaches. They reported that carbon nanotubes (with effectiveness in 170 mg/g) and nZVI (with effectiveness 60–90 mg/g) could be potentially used for nanoremediation of Cr(VI). Among other nanomaterials tested, zeolites and carbon dots also showed positive results, though with lower efficiency (Azeez et al. 2021).

9 Conclusion

Nanoremediation has opened a new possibility to use the uncultivable, heavy metal polluted land. Small-scale application of these remediation methods are tested for treating arsenic, chromium (VI) and other heavy metal toxicity. Out of all the nanoparticles, nZVI appears to be the most promising and cost effective one. However, wide scale applications of these nanoparticles are still limited by the factors like:

- Expenditure
- Technology
- Lack of understanding of their effect on living organisms

With further research, this could turn out to be a key prospect for remediating heavy metal-contaminated soil. Nanoremediation by using zero-valent iron has been approved by U.K. government for applications at about 100 chromium-contaminated sites. Countries making extensive use of this technology mostly include developed countries like USA, Canada, Denmark, Netherlands, Switzerland, Belgium, Spain, France, Portugal, Germany, Hungary, Italy, Israel, Czech Republic, and Taiwan (Bardos et al. 2018). Unfortunately, high cost of nanoparticles has hindered their application in under developed and developing nations. With alarming increase in heavy metal contamination across densely populated countries like India, China, Africa, and other Southeast Asian countries, a cost reduction in the manufacture of nanomaterials should be the future goal. Optimization of the manufacture process, obtaining sources by regenerating scraps and identifying techniques for reusability, could be plausible options to reduce the production cost.

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Phytobial Remediation: A New Technique for Ecological Sustainability

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1 Introduction

Phytoremediation is a method for degrading, stabilizing, or removing contaminants using plants. It may be a green technology option for land, water, and air remediation. Phytoremediation is described as plants usage to eliminate contaminants from the atmosphere or make them harmless as a green technology alternative (Fernández-Luqueño et al. 2017). There are different key techniques in this procedure (Fig. 1) (a) phytoextraction, also known as phytoabsorption, phytoaccumulation, or phytosequestration, is a process in which plants eliminate contaminants from the soil and accumulate them in the plant's harvestable sections. (b) phytodegradation/phytotransformation is the process where contaminants are broken down to simpler compounds by plants and they are combined with tissue, promoting its growth; (c) phytofiltration/rhizofiltration, in which contaminants are absorbed, adsorbent, concentrated, or precipitated by plants or roots; (d) phytohydraulic, which uses plants to upsurge evapotranspiration and restrict the movement of contaminants with water; (e) phytostabilization/phytoimmobilization, where plants immobilize or prevent contaminants from migrating, reducing their mobility and bioavailability in the setting; (f) rhizodegradation/phytostimulation is a process where the microbial activity present in rhizosphere is boosted by the compounds released by the roots of the

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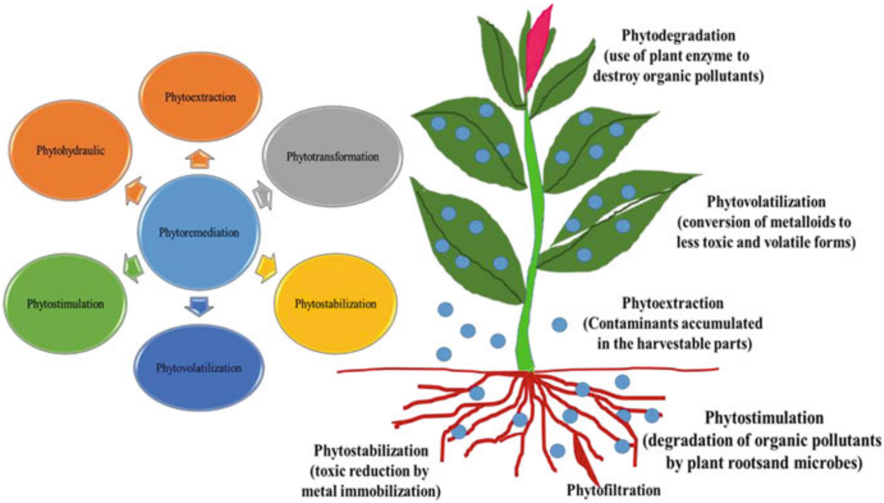


Fig. 1 Different techniques used for phytoremediation

plant across rhizospheric plant groups and soil associated microorganisms; (g) phytovolatilization is the process where, in order to boost the volatilization of pollutants into the atmosphere, plants exploit their ability to absorb, disperse, and subsequently transpire volatile toxins. These remediation techniques are advantageous as well as adheres some weakness, as tabulated in Table 1.

The microorganisms along with plants supports the Phytobial remediation (Lynch and Moffat 2005). Currently, environmentally friendly plant extract facilitated nanomaterial synthesis is being further used for novel environmental remediation purposes. As a result, various species have produced a variety of organic or inorganic nanomaterials that are benefitted in pioneering environmental expertise. Until now, a number of biologically derived inorganic or organic nanomaterials have helped to reduce toxic emissions (Pratibha et al. 2020a). Using phytonanotechnology for environmental remediation, primarily by transformation, adsorption, catalytic reduction, and photocatalysis in biochemical compounds produced by plants. The different aspects of the nanoscale materials for the environmental remediation are discussed in this chapter.

2 Phytosynthesis of Nanoparticles

Nanotechnology refers to the application of phenomena that occur at the nanoscale in the design, manufacture, characterization, and application of materials, structures, fabrication of devices, and systems in science and engineering fields. Nanotechnology is one of the most rapidly progressing fields of technology and has opened up numerous frontiers of research. Nanoparticles are combined in sunscreens and other

Table 1 Phytoremediation techniques with their definition advantages, and disadvantages

Techniques	Definition	Advantages	Disadvantages
Phytoextraction	Pollutants are absorbed by plants and stored in plant parts that can be harvested, such as roots, stems, and leaves E.g.: Sunflower, rapeseed, Indian mustard, and other crops	1. It comes at an affordable price 2. Pollutants are eliminated from sites indefinitely	1. Hyperaccumulators usually have sluggish growth rates, low biomass, and shallow root systems 2. Biomass harvesting necessitates suitable dumping
Phytostabilization	Plants immobilize or precipitate contaminants in the root region, limiting their mobility and bioavailability E.g.: Grasses, prevents soil erosion; willow and poplar trees can retain water; and plants with thick roots confronts the mobility of contaminants	1. Hazardous biomass does not need to be disposed of 2. Plant reduces soil erosion and water availability	1. Contaminants persist in the environment 2. Consistent supervising is needed
Phytodegradation	With the help of the metabolites and hydrolytic enzymes plants degrade organic contaminants. Toxins and recalcitrant organic compounds have been effectively metabolized or degraded using poplar trees (*Populus*) E.g.: Cottonwood, poplar, alfalfa willow, clover, fescue, cowpeas, and *Sorghum*	1. It is not reliant on rhizosphere-associated microorganisms 2. Degradation is aided by plant enzymes	1. It is restricted to the decomposition of organic contaminants 2. It is ineffective in cases of deep contamination, but it is effective in cases of shallow contamination
Rhizofiltration	Via their root systems, plant roots consume, collect, or precipitate toxins from wastewater *Eichhornia crassipes*, *Pistia stratiotes, Hydrocotyle umbellata,* and *Lemna minor* are examples of such plants	1. The majority of the plants used are aquatic, although terrestrial plants are still used occasionally 2. Not necessary to move the heavy metals to shoots	1. Ideal pH level has to be maintained 2. Nursery grown plants are transferred later to the remediation places
Phytovolatilization	Pollutants are converted to a volatile state and then released into the atmosphere Cottonwood, poplar,	1. Contaminants can be converted to the reduced destructive forms 2. Contaminants	1. Contaminants can build up in plants 2. Plant tissue has been shown to contain

(continued)

Table 1 (continued)

Techniques	Definition	Advantages	Disadvantages
	grasses (rye, Bermuda, *Sorghum*), legumes and willow are only a few examples	discharged into the environment are significantly weakened and are less hazardous	low levels of contaminants

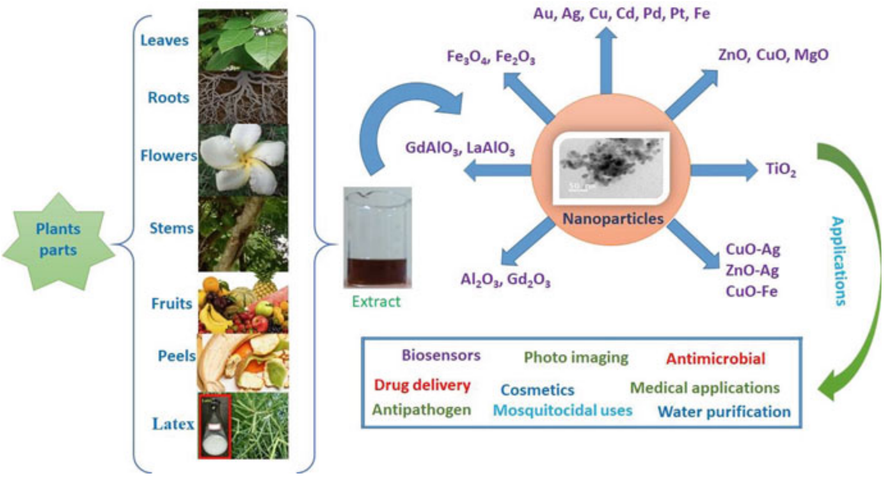


Fig. 2 Various nanoparticle syntheses from plant extracts and their applications in different fields

cosmetics as anti-refelectants and antioxidants. Nanoparticles are benefitted for profitable applications, which are obtained through physical, chemical, and biological methods; these nanoparticles attach firm to the surface, and the possibility of separation and triggering health concerns is minor. Furthermore, the nanoparticles are widely utilized in commercial commodities ranging from paints to personal care products. The dangerous consequences of nanoparticles existing in consumer products are anonymous and remain under investigation.

It has major applications in targeted therapeutic actions, drug delivery, and as biosensors. The biosensors developed through this technology are useful in detecting existence of very small amounts of volatile compounds, pathogens, toxins, and different organic compounds present in body fluids and in various ecological samples, which are in turn use full in areas, such as food processing, recognition of bioterrorism agents, scrutinizing of human diseases, and evaluating efficiency of remediation process. The field of nutrition and nutritional enhancements also involves the nanotechnology. Nanotechnology suggests numerous novel, enriched, and effective approaches for purifying water (Fig. 2) (Pratibha and Chethan 2022; Raveesha et al. 2021; Begum et al. 2020; Begum et al. 2022). Nanomedicine is very important in healthcare segment in remedying different prolonged diseases; therefore, viable synthesis of nanoparticle is believed as building blocks of the upcoming generations to regulate several diseases. Nanotechnology will offer prospects to assimilate science and technology with humanities and social service.

Photocatalytic wastewater purification is a process that combines heterogeneous catalysis with sun energy. In addition to water and air purification, semiconductor photocatalysis with a main emphasis on TiO_2 has been applied to a number of environmental concerns. Hazardous organic compounds can be mineralized to water, carbon dioxide, and simple mineral acids using the photocatalytic method. The solar photocatalytic technique can also be used to eliminate noxious taste, odors, and related compounds, and naturally occurring organic debris, all of which contain the precursor to trihalomethanes generated during water treatment.

For thousands of years, medicinal plants have been used to treat health disorders; to prevent disease epidemics, it is also used in flavoring and conserve food. Plants produce a variety of chemical substances that do not appear to play a direct part in their growth. Secondary metabolites are the name for these substances. These substances contain flavonoids, terpenoids, alkaloids, tannins, and pigments, among other things. Secondary metabolites have physiologic impacts on lipids, hematopoietic cells, and cardiovascular systems, including anticancer, anti-inflammatory, and contraceptive properties. The use of medicinal herbs is seen to be extremely safe, as there are no serious adverse effects. The fact that these medicines are in tune with nature is their primary advantage, and they may be used by people of all ages.

3 Lethal Features and Risks to the Ecosystem

Owing to the increased human population and the fact that present food production rate is insufficient to feed such a huge population, new and novel food production methods involving unconventional technologies, such as nanotechnology, have been required. This technology makes materials having at least one of their dimensions in nanometer scale and bearing the exclusive properties. A novel division of research known as phytonanotechnology has emerged as a result of this new application, in which nanotechnology is combined with plant science to collect the population's food needs. The properties of nanomaterials are advantageous for fertilizer and pesticide application and discharge. These agricultural products must be used in accordance with the dietary requirements and crop health requirements. As a result, the prime advantage of nanotechnology in cultivation is that it decreases the frequency at which these compounds are applied, lowering costs and reducing negative environmental impacts (Pratibha et al. 2020b). However, because of the physicochemical characteristics that distinguish nanomaterials, some researchers have substantiated their potential risks to the environment and human health (Samei and Sarrafzadeh 2019; Wu et al. 2017; Hanot-Roy et al. 2016; Kachenton et al. 2018; Canli et al. 2018; Li et al. 2016). Because of their small scale, they have been shown to be able to penetrate a variety of plant tissues, including roots, leaves, and reproductive organs. Several studies are currently underway to look into the impact of these nanomaterials on cultivation of various plants. Numerous studies have

Table 2 Nanoparticles applications in treatment of drinking water

Nanoparticles	Uses
Nano ag and nano TiO_2	Decontamination or disinfection of organic materials
Magnetic materials	Local remediation
Nano metal ions and metallic oxides	Heavy metals and arsenic removal
Nano iron (zero-valence)	Hydrocarbon, perchlorates, chlorinated remediation

found that plants subjected to treatment of TiO_2 nanoparticles have a major impact on seed germination, biomass production, and, in particular, the growth of the roots of *Panicum virgatum*, *Ocimum basilicum*, and *Nicotiana tabacum* (Table 2). Furthermore, reducing the hereditary appearance of micro-RNA accountable for controlling the abiotic stress withstanding ability has resulted in the identification of many genetic alterations. Similarly, this NP form has been shown to reduce the quantity of starches and chlorophyll intensity in basil plants. As the food chain may get influenced by these nanoparticle-contaminated foods and the packaging components (Lekamge et al. 2019), this raises concerns for human and environmental health. Despite all the recent researches explaining the negative impact of the nanomaterials in various species, there exist an uncertainty regarding the risking of the ecological protection and human welfare which might be due to the excessive discharge of these nanoparticles to the ecosystem. In order to compare and understand the interactions of the compounds with the environment, it is more significant to perform a thorough estimation of the destructive causes of these nanomaterials in a practical setting. Ecotoxicological studies should take into account biotic and abiotic causes, as well as nanomaterial bioavailability and toxicity (Gogos et al. 2016).

4 Nanoparticles for Drinking Water Treatment

Nanoparticles with a large surface area are used for the purification treatment of the drinking water. Antimicrobial properties of silver and copper nanoparticles are the innovative approaches for purifying the drinking water that includes nanotubes, nanoadsorbents, and nanocomposites. Magnetic nanoparticles may also be scattered on the groundwater surface, with magnetite (Fe_3O_4) being the most common, and ferrite nanoparticles (Santhosh et al. 2019). The nanoparticles adhered with the pollutant components can be extracted by the magnetic field, the above are in situ technologies that can minimize operational and transportation costs. Because of their photocatalytic properties, titanium or titanium dioxide nanoparticles (TiO_2), Ag, Cu, etc. are extensively utilized for treating the drinking water (Table 2). While innovative techniques are being investigated and revealed, better technologies are desirable for this serious resource. The possible toxicity of nanoparticles and nanomaterials in water for humans must be considered, as well as the risk of absorption by aquatic species (Gehrke et al. 2015).

5 Nanofertilizers

At present, nanoagriculture refers to the use of nanoencapsulated traditional pesticides, herbicides, and fertilizers, in the gradual and continuous discharge of agrochemicals and nutrients to plants, ensuing in specific dose (Duhan et al. 2017). Agronanobiotechnology is the combination of nanotechnology, biotechnology, and agronomy. Agronanobiotechnology is a field that develops and applies nanotechnology tools to the investigate the agronomic and biological activities (Fernández-Luqueño et al. 2018).

Nanoparticle-based formulations, also known as nanofertilizers, can be characterized as nanoparticles or nanomaterials that deliver advantageous plant nutrients at the nanoscale to promote the growth of plants and also boost the yield (Liu and Lal 2015). The benefit of controlling and the capability to alter physical and chemical properties such as shape, surface composition, structure, scale, load, or various types of nanofertilizers have been extensively expended to upsurge seed germination, improve plant development and harvest, and attain plant safety (Du et al. 2017). Nanofertilizers appear to have the potential to discharge nutritional components in a regulated mode (slowly or quickly) in response to environmental changes, such as temperature, soil acidity, and moisture, enhancing plant growth more effectively than conventional fertilizers (Siddiqui et al. 2015). It is also reported that some nanoagrochemicals could display considerably greater properties comparative to non-nanoanalogs, below research laboratory circumstances (Kah et al. 2018). Furthermore, variations in toxicological efficiency gains reported in the lab have not always been verified for diverse target plants/organisms, and are not promised to occur in the field. Other scientists, on the other hand, argued that nontarget plants and species had conflicting findings (Rajput et al. 2017), but this may have been due to the noxiousness of some micronutrients at greater concentrations than the recommended dose. Carbon nanotubes (CNTs), Ag, Cu, Mn, Zn, Mo, Fe, Ti, Si, and nanoformulations of traditional agricultural efforts including azadirachtin, urea, phosphorus, validamycin, sulfur, and tebuconazole have all been transformed into nanopesticides and nanofertilizers (Fernández-Luqueño et al. 2014). Nanofertilizers are divided into three groups based on plant nutrient requirements: (a) macronanofertilizers (P, N, K, S, Mg, and Ca), (b) micronanofertilizers (B, Fe, Cl, Mg, Zn, Mo, Ni, and Cu), and (c) nanomaterials performing as nutrient carriers (Kah et al. 2018). Micronutrients are often applied as soluble salts to N, K, and P fertilizers in minor quantities to aid crop uptake (Liu and Lal 2015). Further nanoparticles, such as CNT structures, Ti, and Ce, are not involved in the basic nutrients for plants, but they have been shown to have beneficial effects on plants (Oloumi et al. 2018).

6 Wastewater Treatment

The greatest problem posed by industrialization is environmental contamination, which poses a hazard to the natural ecosystem (Han et al. 2019). The present issue is the removal of organic contaminants found in primarily in fertilizers, plastics, industrial effluents, pharmaceuticals, and pesticides. The concentration of different organic contaminants has risen in recent years, posing a global environmental threat (Scott et al. 2019). Innovative methodologies are needed for the removal of refractory organic compounds that do not pose an increased risk to the environment. Nanotechnology and biotechnology stand out among these emerging technologies for producing long-term elimination of pollutants throughout treatment of wastewater (Werkneh and Rene 2019). Many nanomaterials have been identified in wastewater treatment studies using nanotechnology, including semiconductors, nanoclay, nanocatalysts, nanoclusters, nanorods, and nanocomposites (Manjunatha et al. 2019b) (Table 3). Since traditional physical and chemical methods are toxic, there is an increasing curiosity in the exploration of the production of phytogenic irresistible nanoparticles as part of the production of sustainable wastewater treatment processes. Biogenic methods, on the contrary, allow for the manufacture of new environmentally friendly nanomaterials by admitting for unrestricted synthesis techniques in ambient situations. Plant extracts are generated and used during the synthesis of metal ions as reducing and limiting agents (Ali et al. 2017).

Table 3 Different technologies for wastewater treatment

Technologies	Nanomaterials	Plants	Results	Ref
Photo catalysis and adsorption	Zero valence iron nanoclusters	*Cupressus sempervirens*	After 6 h in the process, the nanoclusters showed great promise in removing methyl orange, with a 95% performance	Manjunatha et al. (2019a)
Diverse photo catalysis	Ag-CuO and Ag nanoparticles	*Mimosa pigra*	During the study time (4 h), both nanoparticles degraded methyl blue similarly; though, the Ag-CuO yield was more	Elemike et al. (2019)
Photo catalysis	TiO_2 nanoparticle	*Jatropha curcas* L.	Using direct exposure to sunlight the removal efficiency for COD degradation was found to be 82.26% in this photocatalytic treatment. For the removal of Cr, the efficiency was found to be 76.48%	Goutam et al. (2018)
Photo catalysis	CuO nanoparticles	*Ruellia tuberosa*	After 60 min, the efficacy of CuO nanoparticles for crystal violet degradation (at 585–590 nm) observed light blue color changes, but after 120 min, the crystal violet color disappears	Vasantharaj et al. (2019)

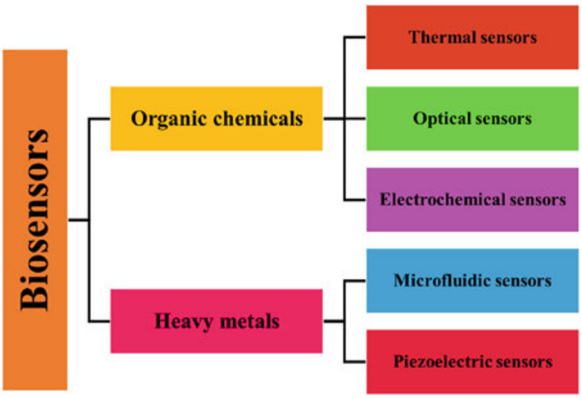
6.1 Nanomaterials as Catalysts

Using nanomaterials, the catalytic contaminant degradation is a more advanced method for environmental remediation that may be reacting for the current requirement of environmental protection (Manjunatha et al. 2019c). The nanomaterials have sparked a lot of interest recently, and advances in nanotechnology have accelerated the growth of nanobiotechnology. Nanomaterials have gotten a lot of consideration as enzyme carriers and restraining agents because of their ability to regulate size and hence offer low mass-transfer opposition and a wide surface area, allowing for enhanced enzyme interaction and thus increasing immobilization performance. The enzyme must be immobilized in a biocompatible surroundings that do not interfere with its natural structure or biological activity (Hwang and Gu 2012). On the surface of the functionalized super paramagnetic nanoparticles, the biomolecules are cultured and loaded. Covalent fixation, regular adsorption, sophisticated combination techniques, and encapsulation are employed in the fixation or incorporation of enzymes (Kim et al. 2006).

6.2 Explicit Detection of Pollutants Using Biosensors in Wastewater

Wastewater treatment procedures that classify the quality of contaminants present are important for long-term sustainability. Biosensors have been divided into five classes based on the broad variety of biorecognition methods available (Fig. 3).They have the potential to detect organic materials as well as heavy metals (Ejeian et al. 2018). The immobilization of the biorecognition factor is critical in the construction of a biosensor, as it can affect the biosensor's electrochemical operation, stability, and repeatability. The recognition factor is a biomolecule that measures biological reaction or physicochemical change and converts it to an electrical signal. Electrodes

Fig. 3 Different types of biosensors used for wastewater treatment



are catalytic biosensors with definite enzyme molecules mounted on transducing surfaces that serve as recognition elements (Campaña et al. 2019).

7 Conclusion

At present, many biologically generated organic or inorganic nanomaterials have degraded toxic compound waste, primarily through photocatalysis, transformation, adsorption, and catalytic bioreduction of biochemical compounds created by plants, a process known as phytonanotechnology. Biotechnology, phytoremediation, and nanotechnology are major front-line wisdom arenas that are combining to provide environmentally sustainable innovations that disintegrate toxins, improve human well-being, and safeguard human and environmental health. This can be accomplished via drinking water and wastewater treatment, through the prevention of diseases and plant pathogens, and synthesizing the sensible nanomaterials used for sensors, nanofertilizer assessment and spread, and pollution detection and dissipation.

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Nanobioremediation: Innovative Technologies for Sustainable Remediation of Environmental Contaminants

Julie Baruah, Chayanika Chaliha, and Eeshan Kalita

1 Introduction

The excessive industrial growth taking place during the nineteenth and twentieth centuries leads to numerous economic and technical advances, continuously shifting the evolution of humanity. The industrial and technological change through diverse activities and products results in the liberation of different contaminants into the atmosphere without adequate precautions (Singh et al. 2013; Wuana and Okieimen 2011). As a result, several difficult cases of contamination caused by effluence have been identified in the past decade. According to World Health Organization (WHO), around 4.2 million deaths per year occurred worldwide resulting from lung cancer, heart disease, stroke, and chronic respiratory diseases caused by pollution (https://www.who.int/teams/environment-climate-change-and-health/air-quality-and-health/ambient-air-pollution). A 2018 study confirms that the byproducts emergent from the combustion of fossil fuel are the world's greatest threat to children's well-being and future, as well as substantial contributors to universal disparities and ecological inequalities (Perera 2018). Innovative technologies have recently been introduced to improve the efficacy of pollutant exclusion. Amid these, techniques of

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bioremediation are a new and efficient tool for cleaning up pollutants in different environments and, as well as a versatile management option to be applied, even on a large scale (Azubuike et al. 2016). Recent studies show that various plant-supported microbes can biodegrade air pollutants (Wei et al. 2017). *Flavobacterium* sp., *Halomonus* sp., and *Arthrobacter* sp. from the plant species *Chinopodium murale* have the ability to biodegrade or convert volatile organic chemicals into less hazardous or benign forms (Ali et al. 2015). Sulfate-reducing bacteria, such as *Desulfotomaculum* and *Archaeoglobus*, also reduce sulfur compounds to hydrogen sulfide (H_2S). H_2S is oxidized to sulfur (elemental) by photosynthetic purple and green sulfur bacteria, as well as certain chemolithotrophs. Sulfate-reducing bacteria then assimilated sulfate into organic sulfhydryl groups (R-SH) (Sun et al. 2005).

Pollution of naval atmospheres resulting from leakage of crude oil at the time of carriage is a major hazard to aquatic lives (Tanzadeh and Ghasemi 2016). In this context, microbial bioremediation of crude oil is more effective than conventional methods, since it is less expensive and does not result in secondary contaminations (Roy et al. 2014). In recent eras, several crude oil-degrading bacteria have been identified on oil-polluted sites. The introduction of non-indigenous oil-degrading microbes into the environment (bioaugmentation) or the stimulation of the indigenous microorganisms' growth (biostimulation) has both been described as successful methods to enhance the detoxification of contaminated sites with insignificant impact on ecological system (Tanzadeh et al. 2020). Even if bioremediation is an excellent versatile recovery technique for various contaminants, it is inefficient while coping with high levels of contaminants, xenobiotics, or recalcitrant materials resulting in unmanageable treatment proficiencies and recovery durations (Mapelli et al. 2017).

In this context, the combination of nanotechnology with bioremediation is advantageous and the method is known as nanobioremediation. This combined approach has enormous potential for being efficient, cheap, and sustainable (Rizwan et al. 2014) to remediate contaminants in groundwater and wastewater (Yogalakshmi et al. 2020), sediments contaminated with heavy metals and hydrocarbons (De Gisi et al. 2017), and either inorganic or organic chemicals in soil (Bharagava et al. 2020). Nanomaterials can have equally positive and negative interactions with abiotic and biotic components, for which several studies have been carried out for evaluating the coactive consequence of nanomaterials and bioremediation practices, as well as explaining their interactions in water and soil (Cecchin et al. 2017).

Nanobioremediation is currently being researched extensively in several polluted area. Nanobioremediation techniques make the ecological pollutants more amenable to biodegradation through biological procedures. Combining biotechnology and nanotechnology is a viable solution for the remediation of environment. Nanomaterials may be utilized alone and in conjunction with microbes (Tanzadeh et al. 2020; Vázquez-Núñez et al. 2020; Yogalakshmi et al. 2020). The microbes/microbial enzymes could be immobilized on nanoparticles or used together with nanoparticles. Recent techniques for nanobioremediation using biologically fabricated nanoparticles, microorganism-assisted nanoparticles, and enzyme-based nanomaterials are discussed in detail in the ensuing sections (Vázquez-Núñez et al.

2020). Furthermore, this chapter will give an overview of the future outlook and challenges associated with the application of these technologies.

2 Nanobioremediation Techniques: Principles

The industries produce around 10 million tons of hazardous chemical substances each year (Thompson and Darwish 2019), which was released into the atmosphere and deposited in soil and remains of water. Deposits resulting through various pathways such as soil erosion, atmospheric deposition, wastewater discharge, rain leaching, and scouring are the primary source of heavy metals (Castillo et al. 2013). Copper (Cu), chromium (Cr), nickel (Ni), arsenic (As), zinc (Zn), lead (Pb), mercury (Hg), and cadmium (Cd) are some of the most common heavy elements found in sediments. Heavy metals returning to the uppermost film of water as the physicochemical properties of the water changed, resulting in secondary pollution. Plants and animals can be harmed by heavy metals, and humans can be exposed to them through the food chain due to a variety of toxicological problems, bioaccumulation, and persistence in the atmosphere (Gong et al. 2018). Various industrial effluents, household wastewater, agricultural overflow, and chemical leaks have a major effect on many water bodies. These effluents contaminate the environment, and the majority of the trash is not biodegradable. They have a detrimental effect on the structure, vitality, and fertility of soils, as well as on human health as well as animals (Abdel-Shafy and Mansour 2018). Chemical pesticides and fertilizers, on the other hand, are being applied to crops in large quantities to increase yield, thereby poisoning the water and soil. The pesticide, insecticide, fertilizer, and pharmaceutical manufacturing generates a significant amount of liquid and solid excess (Brusseau and Artiola 2019). Moreover, these released toxic molecules might react to produce chemicals, such as polychlorinated dibenzofurans or dibenzo-p-dioxins, that are secondary products of some chlorine-based chemical processes (Vázquez-Núñez et al. 2020).

The cytotoxicity of these pollutants and toxic chemical compounds, as well as their various exchanges with abiotic and biotic ecological aspects such as water, plants, animals, microorganisms, minerals, organic matter, and other factors, have implemented effective remediation technology difficult (Jeon et al. 2016; Zhu et al. 2017). Utilization of nanomaterials and nanoparticles in conjunction with biotechnologies could significantly boost remediation capabilities, reducing process intermediates and degradation rates (Kang 2014). Bioremediation involves a variety of techniques, such as bioaccumulation, biosorption, biotransformation, and biological stabilization. These technologies make use of plants as well as microorganisms such as fungi and bacteria, or a combination of the two (Fernández et al. 2018). In recent times, nanomaterials and biological methods are integrated to speed up and facilitate the effective elimination of harmful chemicals from the atmosphere (Singh et al. 2020). Cecchin et al. defined nanobioremediation to describe mechanisms in which nanoparticles are combined with microorganisms or plants to remove pollutants

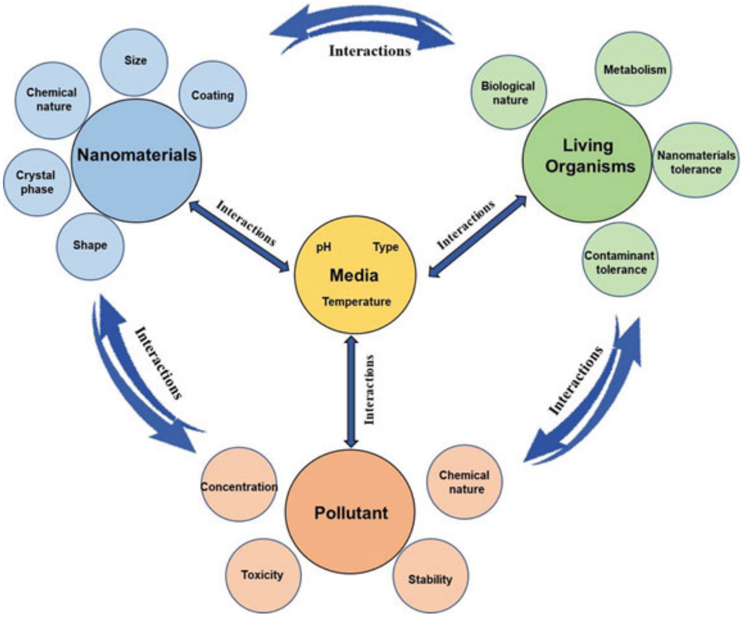

Fig. 1 Effects of various parameters on nanomaterials and live organisms' interactions with pollutants

(Cecchin et al. 2017). Furthermore, based on the nature of the organisms used for remediation, El-Ramady et al. named the procedures with the terminology phyto-nanoremediation, zoo-nanoremediation, and microbial nanoremediation (El-Ramady et al. 2017). The appropriate interaction among nanoparticles and biological organisms is of paramount importance which on the other hand depends on several factors. For instance, the size of nanoparticles, nanotoxicity, and nanonutrition may have an impact on living organisms which in turn has an impact on the entire bioremediation process (Vázquez-Núñez et al. 2020). According to Tan et al., the physical and chemical relations among nanomaterials, biota, and impurities are influenced by several elements like chemical nature, size, and shape of nanomaterials, surface coating, type of contaminants and organism, pH, media, and temperature (Tan et al. 2018). The proper growth of microorganisms, for example, is reliant on temperature and pH media. The nanomaterials or contaminants' stability may in turn be influenced by these parameters. Their interactions are represented in Fig. 1. On the other hand, the physicochemical interactions between nanomaterials, contaminants, and biota are shown in Fig. 2. Different events such as biostimulation, bioaccumulation, and biotransformation may occur when nanomaterials and biota interact that aids in the degradation of pollutants (Taylor et al. 2012). It describes the potential synergistic effect of employing equally nanomaterials and biota in the mitigation processes. In nanobioremediation, both adsorption and absorption processes are essential, where the pollutants may be immobilized, concentrated, and sequestered (Vieira and Volesky 2000).

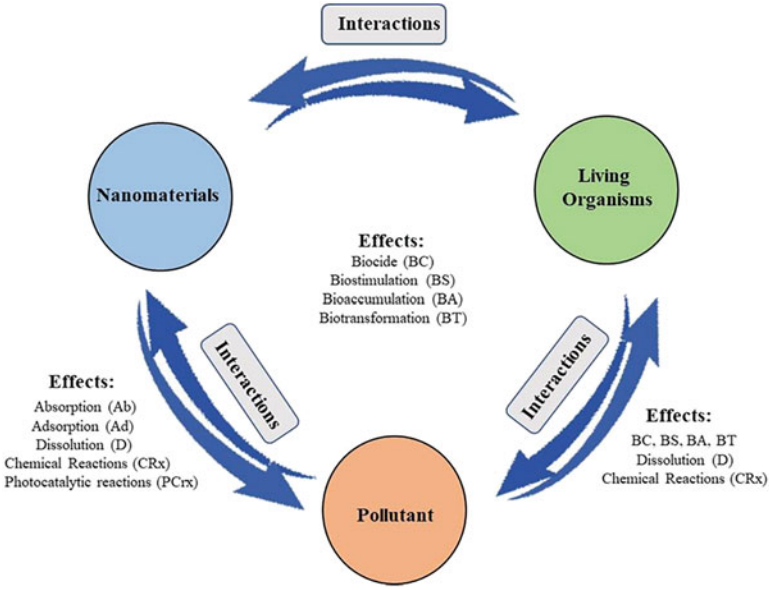

Fig. 2 Various events occurring during nanobioremediation processes resulting from physical, chemical and biological interactions between nanomaterials, living organisms and pollutants

To gain a better understanding of how adsorption works involving nanomaterials, different studies have been carried out. The mechanistic, thermodynamic, and kinetic studies are required to describe the interaction between the nanomaterials with the contaminants. For these, several models such as Temkin and Freundlich isotherms as well as Dubinin–Radushkevich and Langmuir models are explained in the literature (Nath et al. 2016, 2019; Baruah et al. 2020, 2021). Furthermore, pollutants might degraded through photocatalytic procedures depending on the nature of the nanomaterials. Biotic systems can biotransform the resultant products, decreasing pollutant concentrations in the media. Furthermore, several enzymes produced by living organisms have the ability to breakdown a variety of contaminants (Peixoto et al. 2011). Catechol dioxygenases, for example, are enzymes that are the ones in charge of aromatic ring cleavage present in a wide variety of microorganisms that can degrade compounds with aromatic properties (Broderick 1999). Likewise, toxic organic compounds can be detoxified by different fungi and bacteria as well as higher plants through oxidative coupling which is mediated with oxidoreductase enzymes (Karigar and Rao 2011). Laccase is multicopper oxidase enzyme produced by bacteria, fungi, and plants and has been extensively applied for treatment like degradation of resistant dyes and phenols (Datta et al. 2021).

Nanoparticles can reach polluted zones that other entities cannot because of their small size. As a result, nanobioremediation technologies may find new applications. This feature gives it an edge over other remediation methods. For instance, laccase immobilized on nanoparticle composed of iron–copper was discovered to have a higher activity than free laccase. For instance, the immobilized laccase retained up to 61% of its initial action, post ten recycles (Li et al. 2020). Furthermore, it has also been observed that gold nanoparticles immobilized laccase, when forming more stable aggregates, with higher enzyme activity, in comparison with the free enzyme (Suherman et al. 2018). Other considerations are standardization of techniques for measuring the toxicity of nanoparticles or nanomaterials present in water and soil, clarification of their interactions with abiotic and biotic components, and the relevant regulatory framework in which these materials could be used are all important factors (Ramírez-García et al. 2019).

3 Enzyme-Based Nanomaterials in Bioremediation

Enzyme engineering has progressed to the point that we are constantly developing new strategies to solve the majority of the problems that arise in respective area. Enzymes accelerate a wide range of biochemical and chemical responses, and they possess many uses in pharmaceutical manufacturing, diagnosis, biofuel industry, food industry, textile industry, etc. (Karthik et al. 2021). Many enzymes for the removal of pollutants and pathogens have been reported because of their comprehensive research in bioremediation over the last few years, including carboxylesterases, laccases, lysozymes, and haloalkane dehalogenases (Stadlmair et al. 2018; Thallinger et al. 2013). Enzyme-based water remediation is hasty, complex, and maintainable, and several studies have exposed that it outperforms current technologies. It is also a valuable procedure, as enzymes could tailored to fulfil treatment needs at different places (Sharma et al. 2018). Free enzymes are avoided in many industries, because they are difficult to remove or separate from the substance and are lost after the first application. This drawback is solved by immobilizing enzymes, which leads to revolution. Immobilization of enzyme is a procedure that involves imprisoning or confining enzymes in particular medium to limit their liberty of motion (Cipolatti et al. 2016). This process increases the steadiness and function of enzyme immobilization, broadens their pertinence, and provides operation platforms that make this technique more transferable to real-world usages (Sharma et al. 2018). During industrial processes, it also improves tolerance to change in pH and temperature. Other benefits include the simplicity with which enzymes can be isolated from the final product and the ability to reuse the separated enzymes. As a result, the total cost of enzyme-mediated processes is reduced.

Immobilization can be achieved in several ways, as shown in Fig. 3. The chemical bonding method and physical retention method determine how these approaches differ. Since bonding of physical is relatively feeble, it can only hold the reactant binds for a short duration, so chemical bonding is preferred. The carrier material chosen has also an impact on the immobilization mode (Gao and Kyratzis 2008; Jegannathan et al. 2008). Physical trapping, covalent binding, adsorption, and cross-linking are some of the immobilization strategies that can be used using

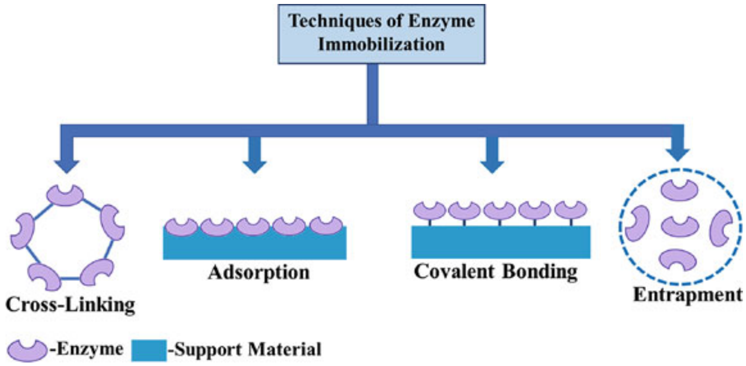

Fig. 3 Different methods used for enzyme immobilization

nanoparticles as transporters (Karthik et al. 2021). Enzymes get caught inside the support in an irreversible process known as physical entrapment. Enzyme would not bind to the polymer chemically. Matrixes for the entrapment process include alginate, silicon rubber, collagen, carrageenan, gelatin, polyacrylamide, polyurethane, and styryl pyridinium group containing polyvinyl alcohol (Guisan 2006). Adsorption immobilization is the mechanism of binding an enzyme to a carrier surface using weak forces, such as the van der Waals force, electrostatic force, hydrogen bond, and hydrophobic contact. A requirement for effective adsorption is the presence of surface of enzyme and carrier with unique efficient moieties (Jegannathan et al. 2008). Enzyme immobilization by covalent binding involves creating chemical bonds among support material's chemical group and enzymes' non-essential chemical group. The side chain of aspartic acids and glutamic (carboxylic group), lysine (amino group), and cysteine (thiol group) is generally used to bond the functional group of enzymes (Soleimani et al. 2012). In the process of cross-linking, the biocatalysts are attached using bifunctional and multifunctional ligands that serve as linkers. This is often referred to as carrier-free immobilization, since the enzymes act as their carrier (Datta et al. 2013). Glutaraldehyde is the most widely used connecting agent, since it has more benefits than others, such as being more inexpensive and readily accessible (Hanefeld et al. 2009).

Currently, another alternative solution is to use nanoparticles as immobilization carriers. Attachment of cells or trapping on nanomaterials greatly improves the bacterial processes of environmental cleaning and facilitates regeneration (Xu et al. 2014). Fungi are often used in wastewater bioremediation. The number of experimental methods for eliminating environmental contaminants using fungal biomass, enzymes, and nanoparticles has greatly increased (Anjum et al. 2019). Magnetic nanoparticles (MNPs) have received a lot of consideration as immobilization transporters for microbes in sewer water remediation because of their large surface area and unusual superparamagnetism that is simple to separate. The magnetic property of a particle has a significant impact on the physical characteristics of water pollutants and aids in water decontamination (Husain 2016). Fe_3O_4

nanoparticles, for example, are successful in the degradation of organic contaminants VOCs, NO, Congo red-eye, azo dye, orange-II, 4-chlorophenol, and PAHs. The ability of biogenic magnetite nanoparticles to adsorb metal cations is approximately 30- to 40-folds greater than that of marketably accessible magnetite. Such characteristics construct them suitable for microbial magnetite production in the elimination of hazardous water metal cations (Ali et al. 2019; Yogalakshmi et al. 2020). Xu and his colleagues used Ca alginate and iron oxide MNPs to immobilize *Phanerochaete chrysosporium* (*P. chrysosporium* immobilized with MNPs–Ca alginate). This was discovered to be an efficient biosorbent with high adsorption potential for Pb(II) removal (185.25 mg/g) than free *P. chrysosporium* and unpolluted MNPs (Xu et al. 2013). Nanoparticles of iron oxide have tremendous potential as wastewater remediation agents because of their high adsorption ability, chemical inertness, and superparamagnetism. Fe_3O_4 MNPs can increase the development and activity of degrading enzymes and are responsible for increasing the permeability of the membrane. Photosynthetic bacteria (PBS) were immobilized on Fe_3O_4/biochar nanocomposites with higher adsorption ion potential (5.45×109 cells/g). The PBS/Fe_3O_4/biochar agent eliminates 92.1% of PO_4^{3-}, 87.5% of NH^{4+}, and 83.1% of COD. In addition, the ability of the composite to remove nutrients was found to be successful post five series (He et al. 2017). Since herbicides can be converted into non-toxic/less toxic inorganic compounds by a variety of microorganisms. *Burkholderia pickettii*, *Pseudomonas* spp., *Comamonas* spp., and *Klebsiella pneumoniae* are well-known examples of bacterial organisms (Seeger et al. 2010; Kumar et al. 2018). Shi et al. found that sulfonamide antibiotics were efficiently removed by nanoparticle-immobilized laccase (Shi et al. 2014). The most well-studied example is the use of laccase immobilization on NPs for environmental cleanup. Laccase, a multicopper oxidase (benzenediol:oxygen oxidoreductase, EC 1.10.3.2), is known to catalyze the conversion of aromatic amine and phenolic substrates. Laccase could degrade certain nonsubstrate dyes in company of insignificant molecular redox intermediaries. Such as, magnetic Fe_3O_4/SiO_2 nanoparticles have been used for immobilization of laccase to decolorize azo dyes (Wang et al. 2013). Laccase nonsubstrate dyes, azophloxine, and Procion Red MX-5B have been used for this. It was able to bleach 80% of equally the dyes, whereas non-immobilized laccase could not. *P. sanguineus* was immobilized over a copper tetra-aminophthalocyanine–Fe_3O_4 nanoparticles that enhanced the storage and thermal steadiness of laccase exceptionally (Huang et al. 2006). For wastewater treatment, a novel combined method of *P. chrysosporium* secretion oxalate and Fe_3O_4 nanoparticles was synthesized that successfully degrades phenol through the coupled photocatalytic–biological process under solar light. According to their proposed mechanism, when exposed to sunlight, the composite reacts to create hydroxyl radical (OH) with high redox potential that enhanced the degradation of phenol (Huang et al. 2015). A possible immobilizing transporter with α-Fe_2O_3 MNPs was created to immobilize *B. ensimensis* and *B. badius* that are atrazine-degrading bacteria. The bacterial cells were found to be distributed uniformly according to the scanning electron microscope (SEM) images. At a wide range of pH 4.0–9.0 and temperature at 20–45 °C, the bacterial cell that is immobilized could withstand a wide range of concentrations of atrazine (50–300 mg/L). Moreover, the cell that was immobilized could also degrade 90.56% of atrazine in just 20 days. Likewise, Fe_3O_4 MNPs were recently immobilized with peroxidase enzyme and improved using glutaraldehyde co-precipitation. Peroxidase is a key enzyme for breakdown of azo dyes and related phenolic composites. In a lab-scale bioreactor, MNPs immobilized with peroxidase effectively bleach colors of various chemical characteristics and are useful for textile effluent remediation (Darwesh et al. 2019). In addition, nanoparticles of TiO_2 were found to be probable candidates for immobilization due to their intriguing characteristics like physical and chemical steadiness, low toxicity, high mechanical strength, great biocompatibility, and cost-effectiveness. TiO_2 nanoparticles are an effective photocatalyst in the removal of different organic contaminants, such as herbicides, pesticides, chemical fertilizers, and insecticides. TiO_2 is also a well-known semiconductor catalyst capable of photocatalytically degrading organic compounds into non-toxic inorganic compounds. Nanoparticles of nitrogen-doped TiO_2 that have been immobilized in *P. chrysosporium* were used to remediate effluent that contains cadmium and 2,4-dichlorophenol (2,4-DCP). Immobilization process increases the toxicity tolerance of *P. chrysosporium* and reduces the treatment time (Chen et al. 2013). *P. chrysosporium* that was immobilized with nitrogen-doped nanoparticles of TiO_2 has also been employed for the remediation of landfill sludges through a short ratio of biodegradability (BOD_5/COD), i.e., 0.09 (Hu et al. 2016). *Pleurotus ostreatus* degrades bisphenol A (BPA) more efficiently in the existence of H_2O_2, according to Li and Zang. According to them, *P. ostreatus* produced extracellular Fe^{3+}-reducing chemicals, which efficiently produce OH radicals. BPA degrades more quickly when the amount of active OH is higher (Li and Zhang 2016). Jiang et al. used nanoscale Fe_3O_4 to entrap *Debaryomyces* sp. in Ca–alginate beads to remediate industrial effluent that contain phenol. Under harsh conditions, *Debaryomyces* strains immobilized with Fe_3O_4 nanoparticles had improved biodegradation efficiency than free cells, with 99.9% of phenol degradation within 80 h. During the same periods, the degradation efficiency of immobilized cells without nano-Fe_3O_4 and free cells was 81.3% and 34.5%, respectively (Jiang et al. 2017). Some recent examples of the production of enzyme-based nanomaterials involved in the remediation of different contaminants are discussed in Table 1.

4 Biologically Fabricated Nanoparticles in Bioremediation

Apart from specifically producing nanoparticles from microorganisms, microorganisms aid in the advancement of nanotechnology in bioremediation in a variety of ways. For instance, microbial enzyme–nanoparticle conjugate, microbes used as biosurfactant on nanoparticles, and immobilization of microbial enzymes on nanoparticles, etc. help in treatment of a broad series of environmental contaminants (Mandeep and Shukla 2020). A nanoparticle–enzyme composite is developed by the immobilization of enzymes within the nanoparticles imparting distinct properties to

Table 1 Different enzymes immobilized in different matrices involved in bioremediation

Enzymes	Source of enzyme	Matrix for immobilization	Molecules targeted	References
Laccase	*Pleurotus ostreatus*	Fe_3O_4/SiO_2 nanoparticles	Procion red MX-5B	Dai et al. (2016)
Laccase	*Aspergillus oryzae*	Magnetic nanoparticles	2,4-Dichlorophenol phenol and 4-chlorophenol	Qiu et al. (2020)
Laccase	*Trametes versicolor*	Magnetic bimodal mesoporous carbon	p-Chlorophenol and phenol	Liu et al. (2012)
Laccase	*Trametes versicolor*	ZnO and MnO_2	Alizarin red S dye	Rani et al. (2017)
Laccase	*Pleurotus ostreatus, Trametes versicolor*		PCBs (polychlorinated biphenyls)	Torres-Duarte and Vazquez-Duhalt (2010)
Peroxidase	Ginger	Polypyrrole–cellulose graphene oxide nanocomposite	Blue 4	Ali et al. (2018)
Lignin peroxidase	*Pleurotus ostreatus* (PLO9) and *Ganoderma lucidum* (GRM117)	Carbon nanotubes	Remazol Brilliant Blue R	Oliveira et al. (2018)
Laccase	*Trametes versicolor*	Metal-chelated chitosan-based nanoparticles	Phenol	Alver and Metin (2017)
Horseradish peroxidase		Carbon nanosphere	2,4-Chlorophenols, bisphenol A, and 4-methoxyphenol	Lu et al. (2017)
Horseradish peroxidase		ZnO nanowires/macroporous SiO_2 composite	Acid Black 10 BX, and Acid Blue 113	Sun et al. (2017)
Laccase	*Trametes versicolor*	Hollow mesoporous carbon spheres	Tetracycline	Shao et al. (2019)
Glycerophosphodiesterase (GpdQ)	*Enterobacter aerogenes*	Magnetic nanoparticles	Organophosphate pesticide	Daumann et al. (2014)
Laccase	*Trametes versicolor*	Tubular mesoporous silica with ultrasmall superparamagnetic iron oxide nanoparticles	Methoxychlor	Yang et al. (2016)
Manganese peroxidase	*Phanerochaete chrysosporium*	Magnetic chitosan beads	Dyes (textile effluent)	Bilal et al. (2016)
Laccase	*Trametes versicolor*	Multi-walled carbon nanotubes	Bisphenol A	Pang et al. (2015)

the nanoparticles. Studies have been performed on a variety of nanoparticles, including carbon nanotube, graphene, and metal nanoparticles biofunctionalized with different enzymes, wherein the properties of the nanocomposite are governed by enzyme categories, active sites of enzyme, physical properties, the morphology of enzymes, etc. (Basak et al. 2020). For instance, immobilization of multi-layer graphene oxide nanoparticle by laccase isolated from *Trametes versicolor* was found with adsorption efficiency for exclusion of micropollutant polycyclic aromatic hydrocarbons (PAHs) found in soil and aquatic ecosystem (Patil et al. 2016). Laccase was immobilized on the exterior of stimulated glass beads by chitosan nanoparticles, which could bleach the hazardous industrial dye, Congo red. Ninety eight percent of decolorization efficiency was achieved which was retained up to 25 successive cycles (Sadighi and Faramarzi 2013). Laccase being widely used for treating industrial effluents, and bioremediation has been achieved by immobilizing laccase via covalent binding on magnetic nanoparticle Fe_3O_4 and chitosan nanoparticle. The composite was capable of effectively eliminating 4-choloro-phenol (4-CP) and 2,4-dichloro-phenol (2,4-DCP) with a removal efficiency of 75.5% and 91.4%, respectively, and regeneration efficiency up to ten cycles (Zhang et al. 2020). Furthermore, the study was carried out on carbon shell chelated with Cu^{2+} and Fe_3O_4 core that were immobilized on laccase which was used for degrading synthetic dyes. The degradation efficiency was 81%, 79%, 75%, 88%, 93%, and 99% for brilliant green, crystal violet, reactive blue 19, azophloxine, Procion Red MX-5B, and malachite green, respectively, for the first cycle and was 80%, 71%, 65%, 60%, 78%, and 94%, respectively, after ten cycles (Li et al. 2020). Likewise, Fe_3O_4@SiO_2@polydopamine NPs biofabricated via immobilizing with lignin peroxidase showed higher bioremediation efficiency of organic pollutants when compared to the free enzyme. Hundred percent of removal efficiency was achieved for phenol, tetracycline, dibutyl phthalate, and 5-chlorophenol whereas 65%, 79%, and 73% for subtraction of benzo(α)pyrene, fluoranthene, and phenanthrene, respectively (Guo et al. 2019). In a study carried out by Darwesh et al. (2019), peroxidase enzyme immobilized on glutaraldehyde-modified iron oxide magnetic nanoparticles was found with a high removal efficiency of red and green azo dyes separately after 4 h. However, the time taken to eliminate red and green azo dyes when used in combination was 6 h (Darwesh et al. 2019). Heavy metal removal was achieved by immobilizing the recombinant enzyme cyanate hydratase on iron-oxide-filled magnetic multi-walled carbon nanotubes. The 29.63%, 35.53%, 39.31%, 34.48%, and 84% removal efficiency was obtained for Cu, Fe, Cr, Pb, and cyanate, respectively (Ranjan et al. 2018, 2019). Biodegradation of crude oil was facilitated with bacterial strain *Bacillus licheniformis* used as biosurfactant on Fe_2O_3 and $Zn_5(OH)_8Cl_2$ nanoparticles. The composite was able to biodegrade total paraffin, including iso- and n-paraffins in crude oil samples (El-Sheshtawy and Ahmed 2017). Bioremediation of organophosphates had been achieved with the fabrication of carboxylated multi-walled carbon nanotubes (COOH–MWCNTs) with covalently immobilized organophosphate hydrolase (OPH). Reduction of organophosphates, methyl paraoxon (MOX), was obtained owing to in situ hydrolyses of MOX by the immobilized OPH during the filtration process (Mechrez et al. 2014). A nanocomposite, bacteria-decorated nanocellulose with *Arthrobacter globiformis* D47 was synthesized and used for degradation of organic xenobiotic pollutants. The degradation efficiency of 78.8% and 83.5% was obtained for chlortoluron and isoproturon, respectively (Liu et al. 2018). In a different study, iron oxide nanoparticles were modified with exopolysaccharides obtained from *Chlorella vulgaris* via coprecipitation for the removal of ammonium ion (NH_4^+) and phosphate ion (PO_4^{3-}). The nanocomposite was able to achieve a removal efficiency of 91% for PO_4^{3-} and 85% for NH_4^+ (Govarthanan et al. 2020).

The technique of encapsulation has been used to biofunctionalized nanoparticles, where nanoparticles are entrapped within the biomolecule, ensuring stability and recyclability of different highly oxidized metal ions (Gross et al. 2015; Bezbaruah et al. 2009). In this context, one of the works describes the comparison between bioremediation efficiency of native zero-valent iron (nZVI) and encapsulated nZVI with alginate polymer for the removal of mixed PAH removal from water. PAH removal efficiency of 43–56% was achieved with nZVI, while the bioremediation efficiency was increased up to 50–75% with the use of encapsulated nZVI at the same concentration. Besides enhancing the removal efficiency, the encapsulation of nZVI in Ca–alginate beads mediated the controlling of chemical properties of the nanoparticles (Abdel-Gawad et al. 2016). Over the last few years, the functionalization of metal nanoparticles with nucleic acids has turn out to be an attention of study in the context of bioremediation. However, while DNA is regarded as a one-of-a-kind suitable molecule for the biofunctionalization of nanomaterials, such as gold for PAH treatment, drawbacks associated with its large size and negative charge make it ineffective at sequestering on nanoparticles (Navarro et al. 2008; Basak et al. 2020). This has been solved by employing a variety of DNA attaching active groups, such as the traditional thiol group, which confers a distinct function by forming a strong covalent bond between sulfur and gold (Oh and Park 2014) (Table 2).

5 Microorganism-Assisted Nanoparticles in Bioremediation

Bioremediation is increasingly becoming the standard technique for removing environmental contaminants and is more environmentally safe and cost-efficient than traditional chemical and physical processes. Herein, different nanotechnological pathways are widely explored as an efficient alternative owing to a small size, high surface area, and better chemical characteristics (Baruah et al. 2019). Indigenous microbes being used as an effective means of eliminating environmental toxins and synthesis of nanomaterials from microbes have open up new avenues for eco-friendly remediation of toxins (Gupta et al. 2016). Microorganism-assisted nanoparticle biosynthesis is a green and environment-friendly technique, wherein bacteria, fungi, actinomycetes, and algae are mostly utilized for production of metallic nanoparticles, viz. gold, cadmium, iron, platinum, silver, zirconium, and palladium, metal oxides such as titanium oxide and zinc oxide nanoparticle

Table 2 Bioremediation of different industrial effluents mediated by bio-based advanced nanotechnology treatment

Nanoparticle	Associated microorganism/ biological system	Pollutant removal	Mechanism	Reference
Copper	*Escherichia* sp. SINT7	Azo dye and textile effluent	Adsorption	Noman et al. (2020)
Iron–sulfur	*Pseudoalteromonas* sp. CF10-13	Naphthol Green B dye	Adsorption	Cheng et al. (2019)
Iron oxide nanoparticles	*Aspergillus tubingensis*	Heavy metal [Pb(II), Cu(II), Ni(II), and Zn (II)]	Adsorption	Mahanty et al. (2020)
Gold nanoparticle	*Trichoderma viridae*	Para-nitrophenol	—	Ai and Jiang, (2013), Mishra et al. (2014)
Zirconia nanoparticle	*Pseudomonas aeruginosa*	Tetracycline	Chemisorption and electrostatic interaction	Debnath et al. (2020)
Silica nanoparticle	Actinomycetes	Textile effluent	Photocatalytic degradation	Mohanraj et al. (2020)
Multi-layer graphene oxide nanoparticle	Immobilized with laccase isolated from *Trametes versicolor*	Congo red	Decolorization	Sadighi and Faramarzi (2013)
Magnetic Fe_3O_4 and chitosan nanoparticle	Immobilized with Laccase	4-Choloro-Phenol (4-CP), 4-dichloro-phenol (2,4-DCP), malachite green, crystal violet, reactive blue 19, azophloxine, Procion Red MX-5B, and brilliant green	Adsorption	Li et al. (2020), Zhang et al. (2020)
Fe3O4@SiO_2@polydopamine nanoparticles	Immobilized with lignin	Phenol, tetracycline, dibutyl phthalate, and 5-chlorophenol	Adsorption	Guo et al. (2019)
Glutaraldehyde-modified iron oxide magnetic nanoparticles	Immobilized with peroxidase enzyme	Green and red azo dyes	Adsorption	Darwesh et al. (2019)
Iron-oxide-filled magnetic multi-walled carbon nanotubes	Immobilized with recombinant enzyme cyanate hydratase	Cu, Fe, Cr, Pb, and cyanate	Reduction	Ranjan et al. (2018, 2019)

(continued)

Table 2 (continued)

Nanoparticle	Associated microorganism/ biological system	Pollutant removal	Mechanism	Reference
Carboxylated multi-walled carbon nanotubes (COOH–MWNTs)	Immobilized with organophosphate hydrolase	Methyl paraoxon (MOX)	Reduction	Mechrez et al. (2014)
Iron oxide nanoparticles	Modified with exopolysaccharides obtained from *Chlorella vulgaris*	Ammonium ion (NH_4^+) and phosphate ion (PO_4^{3-})	Coprecipitation	Govarthanan et al. (2020)
Electrospun nanofibrous webs	Encapsulation with *Pseudomonas aeruginosa*	Removal of dye	—	Sarioglu et al. (2017)
Enzyme immobilized nanoparticle	Laccase immobilization isolated from *P. ostreaus*	Degradation of bisphenol-A, and carbamazepine	Oxidation	Ji et al. (2017)

biosynthesis (Prasad et al. 2016). Microbial production of a nanoparticle is mainly categorized into intracellular or extracellular synthesis. During the intracellular production of nanoparticles, transfer of ions through bacterial cells results in forming nanoparticles in the presence of enzymes. The vast secretory components of microorganisms, which are involved in the decreasing and capping of nanoparticles, are primarily responsible for extracellular production (Narayanan et al. 2013).

The synthesis of nanoparticles from microorganisms is widely studied to sequester or remove toxic pollutants from the environment. *Escherichia* sp. SINT7 has been used for the synthesis of copper nanoparticles which were found to be effective against the degradation of azo dye and textile effluent. The degradation efficiency of 83.61%, 97.07%, 88.42%, and 90.55% was obtained for malachite green, reactive black-5, direct blue-1, and Congo Red, respectively, at a concentration of 25 mg/L (Noman et al. 2020). Iron–sulfur nanoparticles, synthesized from *Pseudoalteromonas* sp. CF10-13, were capable of degrading Naphthol Green B dye and other industry effluents through an extracellular transfer of electrons. Here the synthesis of this biogenic nanoparticle was through endogenous production (Cheng et al. 2019). In another study, a strain of *Aspergillus tubingensis* (STSP 25) isolated from the rhizosphere of *Avicennia officinalis* in the Sundarbans of India was used for the synthesis of iron oxide nanoparticles with competent heavy metal [Ni(II), Pb(II), Zn(II), and Cu(II)] removal efficiency of 90% from wastewater. The metal ion removal was mediated by surface adsorption in endothermic reactions, and the regeneration capacity of the synthesized nanoparticles was up to five cycles (Mahanty et al. 2020). The use of exopolysaccharide (EPS) in bioremediation of dyes, heavy metals, etc. received considerable attention due to their efficient adsorption capacity, eco-friendly, and sustainability properties. In a study carried out with non-glucan EPS-605 isolated from *L. plantarum*-605 that can self-assemble into monodispersed nanoparticles, bioremediation was achieved for Mb, Pb^{2+}, Cd^{2+}, Cu^{2+}, and methylene blue. The adsorption potential of EPS-605 against Mb and metal ions was in the direction Mb $>$ Cu^{2+} $>$ Cd^{2+} $>$ Pb^{2+}, that is influenced by ecological circumstances like pH, initial adsorbate concentration, temperature, presence of background electrolytes, and contact time. The synthesized EPS-605 was further used as a reducing agent for the synthesis of Au nanoparticles (Li et al. 2017). Au nanoparticles synthesized by *Trichoderma viridae* as heterogeneous catalyst was obtained with degradation efficiency of para-nitrophenol to aminophenol (Mishra et al. 2014). Bioremediation technology has been used in treating environmentally hazardous iron ore tailing using *Aspergillus aculeatus* (strain T6). In the study, cell-free extract of the *A. aculeatus* strain T6 was used for bioleaching from tailings waste for construction of protein capped nanoparticles. Nanoparticles synthesized biologically were also found to be the source of bioavailable iron which mediated seedling growth of mungbean seed (Bedi et al. 2018). Also, silica nanoparticles synthesized from actinomycetes have shown 80% decolorization of textile effluent through photocatalytic degradation. The isolation of the actinomycetes was carried out from an effluent contaminated site (Mohanraj et al. 2020). In a recent study, zirconia nanoparticles have been synthesized from *Pseudomonas aeruginosa* with bioremediation efficiency for tetracycline from wastewater. The mechanism behind the adsorption of tetracycline contamination in wastewater by zirconia nanoparticles was substantial electrostatic interaction among the of zirconia nanoparticles surface that was protonated and the tetracycline zwitterionic form. The maximum adsorption efficiency of zirconia nanoparticles was figured to be 526.32 mg/g grounded on Langmuir isotherm (Debnath et al. 2020).

6 Current and Future Prospects

Additionally, developments in other domains of nanotechnology, such as medical nanotechnology, may emerge in combination with the aforementioned nanotechnology utilization in environmental biotechnology. Biotechnology may be able to assist in the development of environmentally sustainable nanoparticle functionalization methodologies. According to Gao et al., *Komagataeibacter sucrofermentans* was recently added to the biological toolkit for the production of new functionalized polymers similar to cellulose with convention moieties. Such bacteria are grown in conventional bioreactors and fed glucose with appropriate chemical changes, resulting in biological integration of the polymer. This method avoids the usage of intricate solvents and the development of hazardous residues in the atmosphere (Gao et al. 2019). The functionalization of nanostructures with biomolecules is also a field worth investigating. This method has been validated using cutting-edge laboratory designs influenced by natural molecular phenomena. Bolisetty and Mezzenga have shown that membranes containing activated porous carbon and amyloid proteins were capable of removing heavy metal ions (Bolisetty and Mezzenga 2016). Later, they have altered tertiary assemblies of proteins of milk for generation of amyloid filaments able to trap various ions through cysteine parts due to the harmful amyloid protein development in neurons. The importance in finding a low-cost source of biomolecules was highlighted in this study as a key to this form of growth.

Recent advancements in the field of RNA-based fungicides suggest that the technology may be used to replace conventional biochemical fungicides. Double-strand RNAs are spread through fruits or leaves and trigger expression suppression in the disease by hybridizing with essential mRNAs of fungal pathogens. The small life-span of bare RNAs in the atmosphere, on the other hand, is a significant challenge (Wang et al. 2016). Nanosheets of clay were tested as double-strand RNA defenders and explored to see if they could extend the biomolecules' mean-life and thus their biocidal activity against the fungal disease. While this method was developed to protect aerial plant organs, it is now being used to protect roots (Mitter et al. 2017). The work of Koman et al. (2018) is added instance of urbane nanotechnology systematization to acquire distant data, in which a conclusion illustration was chemically implicit with inorganic fragments to perceive and notify the existence of an analyte in the air, for example, ammonia, soot, and triethylamine. Recently, inorganic devices, such as nanoplastics, have been designed to track abiotic particles. This definition could be expanded to include biomolecules that track the cells' route in effluent treatment plants, as well as immunodetectable pollutants, and activities that are now accomplished by expensive and difficult analyses like HPLC and DNA sequencing (Mitrano et al. 2019). The technical application of oxygen-responsive proteins presented in plants and humans to create O_2 biosensors and derivable genetic routes is an evolving field. They can be modified to prepare functional nanomaterials that can react to O_2 levels stoichiometrically. These principles, which were first demonstrated by proteins, have been established by DNA molecules that can eliminate complicate analytes such as proteins, opening up a whole new world of sensing and purification possibilities (Diederichs et al. 2019; Licausi and Giuntoli 2021).

It is to note that since there is an absence of awareness and authenticated procedures for evaluation of the effect of nanomaterials on human health, bioaccumulation, biodiversity, and biosafety associated with their application are a serious matter. Several international organizations including USEPA, the OECD Working Party on Manufactured Nanomaterials (WPMN), European Observatory for Nanomaterials (EON), and ISO Technical Committee (TC 229) "Nanotechnologies" have developed worldwide collaboration to improve the implementation of existing principles (Rasmussen et al. 2016; Kica and Wessels 2017). Furthermore, the world markets for nanotechnology and bioremediation are anticipated to remain increasing and evolving innovative roles to boost both environmental as well as human routine aspects.

7 Conclusion

While batch experiments have demonstrated the interaction among nanoparticles and microorganisms to degrade pollutants, there is indeed deficiency of knowledge throughout nanobioremediation process on the synergistic consequence of nanoparticles and biotechnologies and by what means these joint technologies respond to pollutants of various types. Perhaps, there are no published safety data on the long-term usage of nanoparticles with microorganisms. Bionanoparticles have a number of benefits over metallic nanoparticles, including the fact that they are biodegradable and have a lower environmental effect. Although existing nanotechnologies might be employed in decontamination methods for soil, water, or air, further profitable manufacturing procedures could emerge. The regulatory framework is a vital consideration when using these kinds of materials. Scientists may help to better understand the interactions between nanomaterials and biotechnologies throughout remediation procedures with changing environmental circumstances and thus provide reasons for more stringent regulation. In conclusion, nanobioremediation has the potential to make a significant contribution to sustainability, since it offers environmental benefits and is less expensive than other technologies. Furthermore, the spectrum of application of nanomaterials, when combined through biological treatments, has shown more efficacy in removal of pollutants, opening up innovative avenues for addressing environmental issues.

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Part V
Ecological Impacts

Nanomaterials in the Human Food Chain

Luís Marcos Cerdeira Ferreira and Fernando Campanhã Vicentini

1 Processing and Additives: Preservatives, Nutritional and Sensory Enhancement

Processing is a crucial step in the food chain to generate a food product suitable for consumption from an agriculture product. Processing modifications can englobe many procedures, which can include cooking, pasteurization, and incorporation of substances for flavor and taste increasing, texture adequation, nutritional enhancement, and extension of shelf life. Thereby, the incorporation of nanotechnological materials in food aims to increment food quality with new solutions for old problems, including biochemical availability of vitamins, short-term freshness, and food products which originally do not taste good. Furthermore, nanotechnology can offer promising commercial opportunities to produce food with new attractive features (Singh et al. 2017a).

Concerning additives incorporation, substance addition, such vitamin and antioxidants, may not be simple, since it can alter organoleptic characteristics of food and decrease customers appreciation; besides, some nutritional supplements or flavor improvers may need special chemical environment conditions to guarantee proper release and delivery of functionality. In this way, nanotechnology can help to achieve enhanced conditions by using nanoencapsulation technologies, allowing additive ingredients to obtain additional protection against unfavorable environmental conditions, improve stabilization, and reduce nutritional loss. Additionally, nanocapsules can offer a controlled release mechanism of active compounds, triggered by specific physicochemical conditions, which increase bioavailability and food nutrition quality without loss of original food characteristics.

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Nanocapsules are structures that interact directly with customers, thereby there are challenges regarding the search for suitable materials with compatible features to perform that interaction effectively, including biocompatibility with no significative toxicity or accumulation, easy metabolization and excretion, ability to deliver active compounds to precise location in a specific rate, maintain active compounds at appropriate concentrations for long-time periods associated with storage, and finally, do not reduce sensorial features of original food product (Singh et al. 2017a; Dan 2016). In this way, a variety of nanocapsules material has been developed for different purposes, including lipid-based nanostructure, nanoliposomes, gelatin nanofibers, carbohydrate and polymer shells, and protein nanocages (Bratovcic and Suljagic 2019). To illustrate the potentialities of different nanocapsules materials, some examples are displayed in Table 1 alongside of their respective applications.

Protein-based nanoencapsulation systems are one of the most versatile groups for substance carrying in food products, presenting suitable properties, such as antioxidant activity, high adsorptivity front other materials, prevention of aggregation events of nanostructures, production of stabilized colloids, and easy acquisition, once protein can be extracted from different sources, being animal protein, such as whey, albumin, and gelatin, more extensively used. However, with the recent increase of consumers adhering to the meatless diets or who need to undergo restrictive diets, protein from vegetal sources like zein, soy, or pea proteins also can be used with the same intention, as well as recombinant proteins and other natural sources (Fathi et al. 2018).

The versatility credited to proteins is associated with their molecular backbones, which can present a variety of functional groups arranged according to their tertiary structure allowing interaction with of different substances, whether hydrophilic or hydrophobic. Moreover, protein quaternary structure can be managed to assemble into adequate templates, including shells, spheres, tubes, and fibers.

Whey protein, for example, is a combination of serum albumin, lactoglobulins, and immunoglobulins isolated from whey with emulsifying capacity and can produce encapsulation systems containing nanoparticles with dynamic delivery mechanisms. Salem and co-authors used whey protein isolate (WPI) nanoparticles as β-carotene and Zn^{2+} carriers and evaluated their releasing mechanisms at simulated intestinal conditions (Salem et al. 2018). Similarly, Yao et al. combined WPI and gum Arabic to produce a hybrid Fe^{3+} ion nanocarrier with increased entrapment due to chelating process of iron by gum Arabic and enhanced gastric stability, with lower Fe^{3+}-releasing rate at this condition, attributed to an additional protection of hybrid material against pepsin catalysis (Yao et al. 2021).

Substance entrapment via gelatin nanoencapsulation offers adaptability to additive substances for different polarity environments, increasing solubility, as proven by Horuz and Belibağlı, which used bovine gelatin type B nanofibers to encapsulate tomato peel extract rich in carotenoids, especially lycopene, a hydrophobic antioxidant. The capsules were generated via electrospinning, a technique used to produce nanosized fibers from charged threads of polymeric solutions drawn through an electric field. The resulting electrospun fibers presented high extract loading capacity

Table 1 Nanoencapsulation materials for food additives

Nanocapsule material[a]	Purpose	Entrapped compound	Additive property	Reference
WPI NPs	Controlled release in gastrointestinal tract	β-Carotene and Zn^{2+}	Multifunctional	Salem et al. (2018)
WPI/gum Arabic NPs	Controlled release in gastrointestinal tract	Fe^{3+} ion	Prevent anemia	Yao et al. (2021)
Ferritin NCs	Increase thermal and photostability	Anthocyanin	Pigment/ antioxidant	Zhang et al. (2014)
Zein@pectin core–shell NPs	Increase water-dispersibility	Curcumin	Multifunctional	Hu et al. (2015)
Lecithin/choles-terol NLs	Reduce bitter taste/ increase public acceptability	Olive leaf extract (oleuropein)	Antioxidant/ antimicrobial	Tavakoli et al. (2018)
Compritol SLNs	Prevent bacterial spoilage in hamburger	Curcumin	Antimicrobial/ multifunctional	Alanchari et al. (2021)
Liquid and solid edible oils/tween 08 NLCs	Nutritional enhancement of milk and orange juice	Cinnamon oil	Antioxidant/anti-inflammatory/ anticarcinogenic	Bashiri et al. (2020)
Ferritin NCs	Enhance water-sol-ubility/thermal stability	β-Carotene	Pigment/ antioxidant	Chen et al. (2014)
Porcine gelatin NPs	Improve water sol-ubility/color stability	carotenoids from canta-loupe melon pulp	Pigment/ antioxidant	Medeiros et al. (2019)
Chitosan NPs	Increase mushroom preservation	Cumin seed oil	Antimicrobial/ antioxidant	Karimirad et al. (2019)
WPI–gelatin NPs	Increase water-dispersibility	Quinoa oil	Antioxidant	Lira et al. (2020)
LMP/WPI hydrogel	Controlled release in saliva	Orange oil	Flavoring	Kwan and Davidov-Pardo (2018)
HSA/SF/GSH NPs	Controlled release in saliva	Menthol and raspberry ketone	Flavoring	Tallian et al. (2019)
Lecithin NLs	Nutritional enhancement of yogurt powder	Vitamin D	Multifunctional	Jafari et al. (2019)
Marine phospho-lipids NLs	Nutritional enhancement	Vitamin C	Multifunctional	Hassane Hamadou et al. (2020)
GSD/GMS–SLNs and NLCs	Nutritional enhancement	Lycopene	Pigment/ antioxidant	Akhoond Zardini et al. (2018)

(continued)

Table 1 (continued)

Nanocapsule material[a]	Purpose	Entrapped compound	Additive property	Reference
Precirol/octyl octanoat NLCs	Nutritional enhancement of beverages	Vitamin D_3	Multifunctional	Mohammadi et al. (2017)
cacao butter/ tween 80 NLCs	Prevent bacterial spoilage	Cardamom oil	Antimicrobial	Keivani Nahr et al. (2018)

[a]*NCs* nanocage, *NPs* nanoparticles, *WPI* whey protein isolate, *LMP* low methoxyl pectin, *HAS* human serum albumin, *GSA* reduced glutathione (γ-l-glutamyl-l-cysteinylglycine), *SF* silk fibroin, *NLs* nanoliposomes, *SLNs* solid–lipid nanoparticles, *NLCs* nanostructured lipid carries, *GDS* glycerol distearate, *GMS* glycerol monostearate

with enhanced water solubility and were able to stabilize the entrapped carotenoids, providing protection against thermal and oxygen-mediated degradation (İnanç Horuz and Belibağlı 2018).

Protein nanocages can be managed to promote multifunctional activity, combining protection and controlled substance release. Ferritin, for, examples, is a 24-subunits protein assembled into a shell-like supramolecular structure with internal diameter varying from 8 to 12 nm, being very suitable for encapsulation uses. Considering this, Chen et al. were able to manage ferritin properties for encapsulation of cyanidin-3-O-glucoside (C3G), a molecule of the anthocyanin class, used as natural broad color spectrum pigment and a powerful antioxidant, but with considerably low thermal and photostability. Preparation and loading of nanocages with C3G is a simple pH-controlled mechanism: at acidic media (pH = 2) nanocages collapses to ferritin subunits, after addition of C3G, the pH of the media is slowly increased to 7.5 using NaOH, and the ferritin nanostructures are restored and loaded with the ratio of 37.5:1 C3G molecules/protein. Thermal degradation kinetic of resulting loaded nanocapsules was evaluated and showed no significant thermal protection of encapsuled C3G. Comparably, photodegradation rate decreased to twofold smaller values compared to free C3G in a UV light exposure assay. Additionally, the pH-dependent protein nanocage breakdown at acidic media can be used as delivery mechanism, with controlled release of internal anthocyanin load in the gastric environment, where the molecule absorption partially takes place (Zhang et al. 2014).

Combinate biomaterials can be used to generate novel nanostructures to increase dispersity of non-soluble substances in the required media. Hu et al. fabricated core–shell nanoparticles based on hydrophobic zein protein and hydrophilic pectin in a core–shell configuration to encapsulate curcumin, a hydrophobic multifunctional additive with antioxidant and anti-inflammatory properties. The zein@pectin nanoparticles were prepared by electrostatic deposition with loading efficiencies superior to 86% thanks to hydrophobic interaction between curcumin and the zein core, as well as presenting good water-dispersibility (Hu et al. 2015).

Lipid-based nanocarriers and natural emulsifiers also function as efficient encapsulation systems to deliver food ingredients with specific purposes. The unique ability of lipids to produce lipid nanoparticles, and supramolecular arrangements, such as micelles and liposomes, offer countless possibilities for encapsulation of either hydrophobic or hydrophilic compounds, as well as intrinsic favorable properties, including biocompatibility, low environmental impact, and ease management for controlled delivery mechanisms (Walker et al. 2015).

Liposomes have been extensively applied in as drug carrier for pharmaceutical use over the past decades. Since they are based on amphiphilic lipids or weak surfactants disposed in a limited concentric bilayer with spherical shape and an internal cavity, their potentialities for substance carrying are wide. When liposomes are produced in nanoscale, some features are amplified, such as bioavailability, as well as their suitability for substance encapsulation in food applications (Akhavan et al. 2018).

Lipid-based nanocarriers are useful to deliver nutritional additives that induce unpleasant sensory experiences, such as polyphenols, which generally have a bitter taste. Tavakoli et al. used lecithin and cholesterol to produce nanoliposomes loaded with olive leaf extract via ethanol injection. The nanoliposome production yielded particles with sized varying from 25 to 158 nm with loading efficiencies higher than 85%. The addition of extract-bearing particles to yogurt samples decreased syneresis rate (expulsion of the liquid phase from the dispersion) at storage conditions and increased antioxidant activity. Additionally, a sensory study was performed using three different samples: yogurt with extract-bearing nanoliposomes, yogurt with free phenolic extract, and a control sample consisting in yogurt without nanoliposomes and phenolic extract. Considering color, taste, and texture as sensory parameters, the nanoliposome enriched yogurt presented scores comparable to the control sample and significantly higher than free extract yogurt (Tavakoli et al. 2018). These results show how nanoliposome encapsulation can enhance nutritional value of food without loss public acceptability.

Other attractive lipid-based nanostructures that can also work as substance carrier include solid–lipid nanoparticles (SLNs), which basically comprise a lipid core capable to solubilize hydrophobic species, generally stabilized by emulsifiers, ant that remains solid at room or physiological temperatures. Similarly, the so-called nanostructured lipid carriers (NLCs) involve a less ordered matrix compared to SLN, being produced by the combination of lipids in solid and liquid phase.

Encapsulation with lipid-based materials allows the incorporation of active spices in food without significant sensory changes, as illustrated by the curcumin-loaded compritol SLNs reported by Alanchari et al. to extend shelf-life of hamburger samples. Curcumin is a popular spice and can be employed to prevent microbial spoilage, but the large amounts of curcumin used for this purpose can result in unpleasant taste for sensible customers. To reduce the possibility of this type of experience, curcumin was encapsuled in the SLNs via microemulsion method resulting in particles with 126 nm approximately with 99.96% of loaded efficiency and enhanced antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* growth (Alanchari et al. 2021).

Liquid food can also be nutritionally fortified using lipid-based nanoencapsulation through NLCs, since the presence of both solid and liquid lipids results in colloidal density close to water and may not alter significantly sensory properties such visual appearance and texture. Considering this premise, Bashiri et al. developed different plant-based edible oils NLCs to deliver cinnamon essential oil in milk and orange juice samples with additional study about stability under pasteurization process and different pH conditions of the beverage models. The cinnamon oil-loaded NLCs were produced by high shear homogenization–ultrasonication, resulting in variable size nanoparticles (100–120 nm) with loading efficiency superior to 82%. Then, enriched NLCs were dispersed in different samples: orange juice (pH 3.8), skimmed milk (pH = 8.3), and whole milk (pH = 6.7), resulting in an increase in particles size and polydispersity (heterogeneity of particles sizes) at the highest pH sample, attributed to aggregation process, but without loss of nanometric dimensions. Pasteurization assay of NLCs dispersions was performed by heating to 65 °C during 30 min and leading to significant but non-compromising changes in particles size and polydispersity. In general, these results showed satisfactory application for nutritional enhancement of beverages (Bashiri et al. 2020).

2 Nanotechnology in Food Analytical Quality Control

Quality control based on chemical and biological analyses is a crucial step in food production, being performed to guarantee the safety of costumer and food industry workers, as well as the food product integrity and consequently avoiding production and economic losses. More than ensuring a nutrition fact label in the final product, analytical quality control is an important tool to attend national and international quality standards and to prevent against eventual risks, including chemical adulterations; additive excessive dosages; contamination with microbial pathogens, such as bacteria, viruses, and fungi; and potentially hazardous substances like antibiotics, hormones, and pesticides. Since contaminations can propagate through all over the production chain, the implementation of analyticalsis routines is necessary in all steps of this chain, which means that the methods and techniques used in these analyses must have proper degree of accuracy and reliability. Moreover, to attend the demand of agricultural and food industries, the analytical procedures must adapt to different conditions of production, which includes the development of less laborious routines, simplified methods, and more important, the possibility of point-of-care (POC) testing using analytical systems based on simple operation portable devices which can be used locally, in crops, corrals, water reservoirs, grain bins, or any place with limited resources, reducing as much as possible the need of laboratorial analysis and saving time (Zhang et al. 2020; Dai and Liu 2019; da Silva et al. 2017).

Despite nanotechnology has contributed to the enhancement of most of conventional analytical techniques and the advent of new methods, due to the current demand for POC analysis, colorimetric and electrochemical analyses will be the main focus here. Furthermore, it is important to notice that the development of analytical sensors is directed to many sectors of food chain, including soil chemical availability in cultivation areas, biological safety, food processing steps, and even in the so-called intelligent packaging, which will be properly discussed in the next section (Manessis et al. 2019; Kundu et al. 2019). In order to present a more concise and detailed vision of sensors application, this section will also emphasize the direct analysis of food and food products.

Considering this scenario, nanotechnology arises as the source of multiples solutions, since the advent of nanostructured materials, such as metallic nanoparticles, graphene, and carbon nanotubes, has brought new perspectives for analytical chemistry and biochemistry. These nano-sized materials are endowed with inherent characteristics, which includes high surface area, stability, easy manipulation for miniaturization (essential for POC analysis), physicochemical interactions toward to signal enhancement, and biocompatibility, acting as a function components for the development of new versatile sensors and biosensors with high sensitivity and specificity to target molecules, being applicable in several transducing systems, especially those based on optical and electrochemical transduction.

A practical example of performance of this kind of sensor can be illustrated by the detection and quantification of adulterants in milk: melamine is a quite common adulterant substance that is intentionally added in milk or milk products. Since melamine is a nitrogen-based compound, it can distort analysis results of protein content by promoting a false protein boost. Moreover, despite its low toxicity ($DL_{50} = 3248$ mg/kg), melamine can be hydrolyzed and converted to cyanuric acid, which the chronic exposition is related to the renal and reproductive damage, formation of bladder and kidney stones. After the Chinese milk scandal in 2008, when the presence of melamine in an infant formula caused the hospitalization of tens of thousands of babies, a warning concerning the need of melamine monitoring analysis in raw milk and milk products was received worldwide (Chen 2009; Gossner et al. 2009).

In contrast to laboratory-performed techniques like liquid chromatography, a practical approach to detect the presence of melamine in milk can be set up using metallic nanoparticles, such as silver or gold, to create a sensing system. These particles are able to produce a visual differentiation of substances through the phenomena of localized surface plasmon resonance (LSPR) that is based on space-confined electrical oscillations over the surfaces of nanoparticles caused by the absorption of an incident electromagnetic radiation. Plasmon absorption wavelengths are intimely related to the size, shape, and aggregation state of nanoparticles. Then, this electrical phenomenon can be manipulated to investigate variations in the nanoparticle's morphology caused by the chemical environment, such as the presence of a contaminant molecule that can induce changes on plasmons oscillation causing a shift in the absorption wavelength. Gold and silver nanoparticles are preferable used in this kind of approach since their resonating plasmon absorption happens in the visible spectrum. In this condition, a color change is observed when the morphological alteration happens, producing a colorimetric probe that can be applied in the detection of melamine, which under controlled conditions, affects the aggregation state of nanoparticles. In this context, several colorimetric methods are reported in the literature based on the systematization of different mechanisms for melamine-mediated aggregation of nanoparticles to generate a controlled LSPR-based analytical system for melamine detection in milk (Chen et al. 2019; Chi et al. 2010; Gao et al. 2018; Kumar et al. 2014, 2016; Song et al. 2015; Yin et al. 2015). Furthermore, functionalization of nanoparticles with molecular agents can increase the sensor performance. Song et al. reported the use of a sulfanilic acid-modified silver nanoparticles (AgNPs) which induced to an increased affinity with the target molecule, achieving a limit of detection at nanomolar level (Song et al. 2015). Similarly, Chen et al. used polyethylene glycol (PEG) to select the interactive area of gold nanoparticles (AuNPs) surface, inducing a specifically oriented aggregation pattern, increasing the stability of the sensor for a longer time compared to non-modified nanoparticles (Chen et al. 2019).

A more sophisticated and accessible approach stands out when this sensing system is incorporated to popular technologies. Gao et al. related the development of paper-based colorimetric analytical device for melamine quantification which the response is read and processed by a smartphone (Gao et al. 2018). In this work, a filter paper was impregnated with a dispersion containing AuNPs modified with Triton X-100 in order to generate a highly stabilized condition against abrupt changes in pH and ionic strength, reducing the occurrence of unspecific aggregation. As can be seen in Fig. 1, the presence of melamine induces aggregation of modified AuNPs causing a shift on localized plasmon absorption peak and resulting in a gradual color change from red to blue. The signal processing was carried out using a simple color-scanning app to register the resulting RGB intensity. The combination of this nanostructure-based device with a common use gadget creates a completely portable way to perform colorimetric analysis of melamine. Moreover, the simplicity of operation allows the analysis to be performed by a non-specialized person in any location, like milk producers or their buyers at dairy farms.

At this point, we can see that colorimetry with smartphone-based readout can be the basis of a wide range of methods for POC analysis and a powerful tool to implement reliable food quality control. In fact, this strategy is highly versatile and can be easily adapted to the analysis of other milk contaminants, including hydrogen peroxide, which is often added to raw milk to increase preservation by preventing microbial spread. However, the slight excess of this substance causes gastrointestinal damage, as well as it reduces milk nutritional value significantly, since it can induce oxidative degradation folic acid (Souza et al. 2011). In this way, given the hydrogen peroxide characteristic to trigger redox reactions and induce morphological changes in metallic nanomaterials, several colorimetric methods are found to detect this contaminant, using metallic nanoparticles combined with natural polymers to enhance optical response and prevent unspecific response (Alzahrani 2017; Teodoro et al. 2019; Lima et al. 2020; Üzer et al. 2017), similar to the melamine approaches, or anchoring molecular dyes on their surfaces, like the device presented by Khachornsakkul and Dungchai, which used tetramethylbenzidine (TMB) attached to AgNPs to initiate a color change reaction to generate analytical response (Khachornsakkul and Dungchai 2020). The presence of hydrogen peroxide triggers the oxidative etching of AgNPs generating hydroxyl radicals (OH·) which oxidizes TMB giving to the reaction media a blue color, and the blue intensity is recorded and

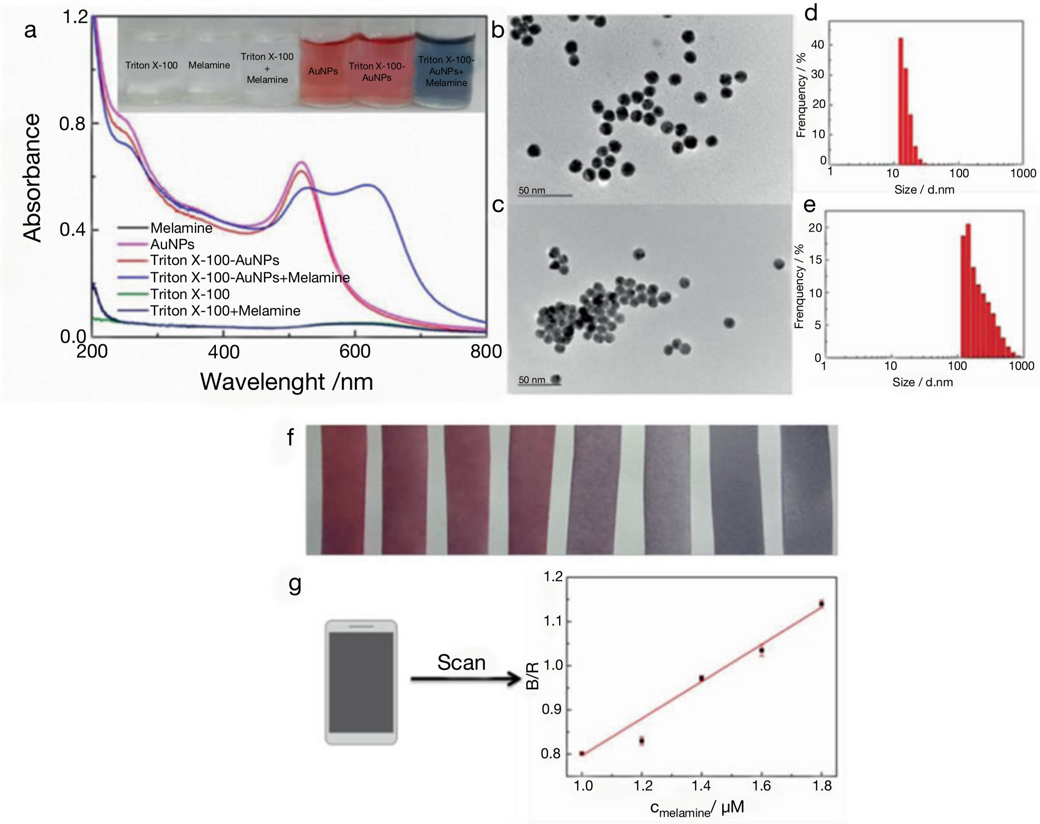

Fig. 1 (**a**) UV–Vis absorption spectra of melamine, AuNPs, Triton X-100-AuNPs in the absence and presence of melamine, and Triton X-100 in the absence and presence of melamine, respectively. Inset is the corresponding photograph. TEM images of Triton X-100-AuNPs in (**b**) the absence and (**c**) presence of 1.75 μM melamine. DLS measurement of (**d**) Triton X-100-AuNPs only and (**e**) in the presence of 1.75 μM melamine. (**f**) Color image of the designed test paper

processed by a smartphone. This device is able to achieve a limit of detection of 2.0 nmol L^{-1}.

Obviously, colorimetric analysis is not always suitable to detect all contaminants of interest. The specific response of some substances on LSPR pattern of nanoparticles depends on certain physicochemical properties that make them very convenient analytical targets. In this way, the detection of any other substances needs to be performed in other analytical platforms, preferably favorable to POC assays, presenting the required simplicity and portability to achieve this condition, and being compatible with physicochemical properties incident in a wide range of substances. In this sense, electroanalytical techniques offer a great advantage due to its simple instrumentation toward miniaturization, since most of these techniques are based on interfacial charge transfer, which takes place at electrodes surfaces, so that the analytical response is not inherently dependent on the transducer size. Additionally, the electrodes used in these techniques are highly compatible with nanomaterials, especially those with substantial electrical conductivity, such as metallic nanoparticles as carbon-based materials like graphene and carbon nanotubes, allowing redox processes with increased charge transfer rates, and consequently, giving the sensor a higher current signal and the sensitivity required to detect contaminants at trace levels, including pesticides and heavy metals (Ding et al. 2021; Wang et al. 2020).

Moreover, these materials are endowed with high surface area and binding sites suitable for the attachment of biomolecules, such as enzymes, antibodies, nucleic acids (DNA or RNA), or any other molecule capable to perform specific interactions with determined target. In this combination, arises the concept of the called nanobiomaterials, which is the basis of the development of high-performance biosensors for food contaminant analysis, particularly when a foodborne contaminant comes from a biological source, including pathogenic toxins or microorganisms. In this context, many electrochemical biosensors have been described in the literature focused on the development of new electrode architectures based on bioactive nanostructured materials (Gupta et al. 2021; Mishra et al. 2018; Miao et al. 2019; Evtugyn and Hianik 2019; Riu and Giussani 2020; López et al. 2012).

Regarding the use of active biomolecules, antibodies comprise an amazing group of proteins capable to perform highly specific biorecognition, and their inclusion in sensorial platforms generates the so-called immunosensor. A good example that illustrates electrochemical immunosensors performance is presented by Yu et al., which have reported the impedimetric detection of aflatoxin B_1 (AFB_1) in olive oil (Yu et al. 2015). AFB_1 is one of the most hazardous substances produced by fungi, being highly hepatotoxic and carcinogenic. To detect this substance at trace levels,

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Fig. 1 (continued) with different concentrations of melamine (0, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2 μM). (**g**) Application of a smartphone in melamine detection using the test paper. Right is the B/R ratio vs. melamine concentrations. (Copyright 2018. Reproduced and adapted with permission from Elsevier B.V. Gao et al. 2018) the proposed sensor consisted in a composite electrode film containing multi-walled carbon nanotubes (MWCNT) and room temperature ionic liquids (RTILs) able to the attachment of anti-AFB_1 antibody. The association of high conducting materials mediated by interactions between the concentric 3D sp^2-network of MWCNT and imidazolium cations of RTILs provided the appropriate sensitivity to detect AFB_1 at the limit of 0.03 ng mL^{-1}. A variety of other approaches using nano-based immunosensor for detection of mycotoxins in food are summarized in Table 1.

Nanostructure-based electrochemical immunosensors are also able to detect the presence of cell organisms, such as bacteria. Electrode surfaces can be modified to detect selectively cells of *Salmonella*, *E. coli*, or any living organism containing a specific biomolecule that can be target. Jia et al. were able to detect *Salmonella* using an aptamer bound to a glassy carbon electrode-modified MWCNT and reduced graphene oxide (rGO) to generate an impedimetric sensor. Aptamers are oligonucleotides produced by a random sequence of nucleotides with the ability to bind to specific target molecules. The amino-terminated aptamer was covalently attached to -COOH groups located in the MWCNT structure, generating a nanobiostructured electrode surface able to detect *Salmonella* cells in chicken samples with limit of detection (LOD) of 25 cfu mL^{-1} (Jia et al. 2015).

A multi-nanomaterial approach presented by Narayanan et al. for detection of the botulinum neurotoxin type E (BoNT/E) used glassy carbon electrode modified with a graphene nanosheet matrix to anchor a first capturing antibody (rabbit–anti-BoNT/E) in order to perform a sandwich immunoassay as follows: after the antigen capture, a second capturing antibody (mouse–anti-BoNT/E) is introduced in the system, which is able to attach to the signal probe consisting in gold nanoparticles functionalized with anti-mouse IgG and alkaline phosphatase (RαMIgG–ALP/AuNPs). At the presence of the enzymatic substrate 3-indoxyl phosphate (3-IP), the loss of phosphate group induces deposition of silver nanoparticles by chemical reduction of Ag^+ ions present in the media, which leads to a signal enhancement, as showed in the mechanism summarized in Fig. 2. The resulting immunosensor was applied in the analysis of milk and orange juice samples and exhibited an LOD of 5 pg/mL using sweep linear voltammetry, demonstrating the multifunctional capability of bionanomaterials applied to electrochemical analysis (Narayanan et al. 2015).

Electrode materials, based on nucleic acids as DNA, are also able to perform very specific interactions with a correspondent genetic material present in a sample. Nanostructured genosensors manufactured for the recognition of base sequences of bacteria arise as stunning sensing platforms for the detection of bacterial contamination in food samples alongside immunosensors (see Table 1). Izadi and co-authors presented a genosensor based on a thiolated DNA probe attached to AuNPs which were supported on a pencil graphite electrode to target *Bacillus cereus* in milk, a pathogen responsible for diarrheal syndrome (Izadi et al. 2016). Similarly, Rahman et al. used nanospheres constituted by a copolymer (polystyrene–co-acrylic acid) to anchor a DNA sequence for *Vibrio cholerae* detection (Rahman et al. 2017). These approaches are faster alternatives compared to conventional cell culture analysis, which are generally completed in a period of days or even weeks.

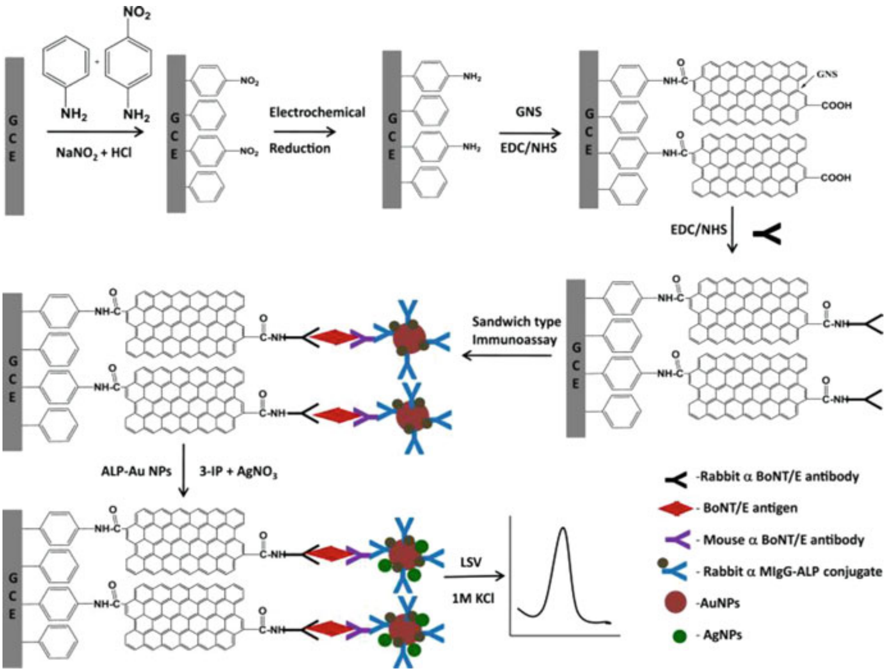

Fig. 2 Steps involved in GC electrode modification and sandwich immunoassay-based detection procedure for analysis of deposited silver nanoparticles (AgNPs) generated by MIgG–ALP/AuNPs catalysts and 3-IP reaction. (Copyright 2015. Reproduced with permission from Elsevier B.V. Narayanan et al. 2015)

Exogenic contaminants, such as pesticides, hormones, and antibiotics are also considered target molecules for biosensors. They are found as residues of other agricultural procedures that aim to reduce microbial contamination and pests that can lead production lost. However, the exposure of customers to those substances is known to be potentially harmful. Glyphosate, for example, is a broad-spectrum herbicide used worldwide for weed control. The use of glyphosate is intimately related to genetically modified organism (GMO) in agricultural production, especially in soybean crops, which are genetically designed to be resistant to glyphosate. Despite some controversial meta-analysis results involving of the World Health Organization (WHO), there is no substantial evidence that confirms the risk of glyphosate exposure to the final customer or to farm workers (Torretta et al. 2018). However, the impact related to the spreading of glyphosate and other pesticides in soil, aquatic environment, and animal life is found to be significative. In addition, the increasing popular demand for “organic” food, produced with no GMOs, pesticides, or any drug for production control, has intensified the need of pesticides analysis and other similar contaminants (Perez-Fernandez et al. 2020; Arduini et al. 2016; Bakirhan et al. 2018). The presence of antibiotics and hormones is also of great concern from consumers about potential health risks and has also motivated the development of new nano-based biosensors for food analysis (Gaudin 2017; Luan et al. 2020; Khan 2022; Pollap and Kochana 2019; Majdinasab et al. 2017; Cifrić et al. 2020). Some few examples of application of these devices are found in Table 2.

Regarding development of biosensors for pesticides detection, the most popular approach is based on the inhibition of enzymes activity promoted by these substances, which creates a universal probing approach for indirect detection, as the sensor presented by Cahuantzi-Muñoz et al., which immobilized the enzyme horseradish peroxidase (HRP) on an MWCNT-modified graphite-epoxy electrode. The electrode response was based on the quenching of current signal associated with the hydrogen peroxide oxidation at the presence of small concentrations of glyphosate. The sensor was applied in the analysis of the pesticide in corn. The increased sensitivity-associated MWCNT-mediated charge transfer allowed to achieve the outstanding limit of detection of 1.32 pmol L^{-1} using cyclic voltammetry (Cahuantzi-Muñoz et al. 2019).

3 Active and Intelligent Nanotechnology in Food Packaging

Food packaging is known to offer protection against physical damage, in addition to provide chemical or biological environment conditions according to foodstuff particularities, and facilitate transport and storage processes. Additionally, they are labeled with basic food information: barcode systems to help identification and purchase process, as well as a set of attractive messages and graphical elements made to draw the attention of the consumer. However, the roles of food packaging have expanded as the increasing need of a higher reliability standards. The use of nanotechnology changed the roles of packaging and brought the concepts of active and intelligent packaging, giving customers (and sellers) a guarantee that the product is appropriate for consumption and a real-time information about what they are buying, or even a real record about what conditions the food had been through.

The concept of active packaging is based on dynamic process to enhance food protection against the arising of conditions which could lead to microbial contamination or food deterioration (rotting or oxidation). The technologies associated with active packaging are often categorized in two dynamic systems: (1) active coating, which uses films containing different materials that function as protective barriers, substance releasing mechanisms to cease microbial growth and control the chemical environment, or absorbing materials that retain substances which can induce degradation process; and (2) sensing systems, or intelligent packaging, designed to detect foodborne contaminants or to register physicochemical variations. In an ideal situation, both systems could be combined to produce systems based on active feedback controlling mechanisms, like substance release, trigged by the sensing response.

Table 2 Electrochemical biosensors based on nanobiomaterials for food contaminant analysis

Contaminant class	Specific contaminant	Nanostructured material[a]	Biorecognition agent[b]	Food sample	Reference
Mycotoxin	Aflatoxin B_1	MWCNT	Ab anti-AFB_1	Olive oil	Yu et al. (2015)
	Aflatoxin B_1	Electrodeposited AuNPs	Ab anti-AFB_1	Corn	Ma et al. (2016)
	Ochratoxin A	AuNPs	Ab Anti-OTA	Red wine	Malvano et al. (2016)
	Ochratoxin A	Zirconia NPs	Ab Anti-OTA	Coffee	Gupta et al. (2017)
	Fumonisin B_1, doxynivalenol	AuNPs/polypyrrole/ErGO	Ab anti-FB_1/anti-DON	Corn	Lu et al. (2016)
	T-2 mycotoxin	AuNP/SWCNT/chitosan	Ab anti-T-2	Swine meat	Wang et al. (2018a)
	Zearalenone	Au@AgPt nanorattles	Ab anti-ZEN	Milk	Liu et al. (2014)
Bacteria	*Escherichia coli*	DNA nanopyramides	Ab anti-*E. coli*	Drinking water	Giovanni et al. (2015)
	E. coli	CdS quantum dots	Ab anti-*E. coli*	Milk	Zhong et al. (2019)
	Salmonella typhimurium	Nonporous gold	Aptamer	Egg	Ranjbar et al. (2018)
	Bacillus cereus	AuNPs	*B. cereus* DNA sequence	Milk/infant formula	Izadi et al. (2016)
	B. cereus	AuNPs	Ab anti-*B. cereus*/HRP	Milk	Kang et al. (2013)
	Clostridium perfringens	CeO_2 nanorods	*C. perfringens* DNA sequence	Milk/milk powder	Qian et al. (2018)
	Vibrio cholerae	PSA-NPs/AuNPs	*V. cholerae* DNA sequence	N.A.	Rahman et al. (2017)
Bacterial toxin	*Botulinum* neurotoxin serotype-A	AuNP/graphene/chitosan	Ab anti-BoNT/A	Milk	Afkhami et al. (2017)
	Botulinum neurotoxin type-E	AuNPs/graphene	Ab anti-BoNT/E; RαMIgG-ALP	Orange juice/ milk	Narayanan et al. (2015)
	Staphylococcus entero-toxin-B	DNA nanopyramides	Aptamer	Milk	Chen et al. (2018)
Pesticide	Glyphosate	Montmorillonite nanoclay	HRP	Corn	Oliveira et al. (2012)

	Glyphosate	AuNPs	Urease	Drinking water	Vaghela et al. (2018)
	Glyphosate	MWCNT	HRP	Corn	Cahuantzi-Muñoz et al. (2019)
	Paraoxon	Prussian blue nanoparticles	Butyrylcholinesterase	Drinking water	Arduini et al. (2015)
	Captan	ZnO nanorods	AChE	Apple	Nesakumar et al. (2015)
	Methyl parathion	AuNPs/SiO_2/MWCNT	Methyl parathion hydrolase	Garlic	Chen et al. (2011)
	Carbaryl	MWCNT/GO nanoribbons	AChE	Cabbage	Liu et al. (2015)
	Formetanate	Electrodeposited AuNPs	Laccase	Fruits	Ribeiro et al. (2014)
Hormone	17β-Estradiol	Graphene/PANI/GO	Ab anti-17β-estradiol/ HRP	Milk	Mazloum-Ardakani and Khoshroo (2013)
	Zeranol	Nanoporous gold/nano-montmorillonite	Ab anti-zeranol (2 types)	Beef liver	Feng et al. (2013)
	Norethisterone	Mesoporous SiO_2 NP/AuNPs	Ab anti-NOR (2 types)/ HRP	Chicken liver	Wei et al. (2010)
Antibiotic	Sulfadimethoxine	rGO/AuNPs	Aptamer	Beef/chicken/ fish	Mohammad-Razdari et al. (2019)
	Neomycin	SWCNT	Ab anti-neomycin	Milk	Wu et al. (2012)
	Chloramphenicol	Cd^{2+}-Pb^{2+}-nanobrushes /magnetic AuNPs	Aptamer	Fish	Yan et al. (2015)
	Tetracycline	PtNPs/graphene	Ab anti-tetracycline	Honey/milk/ peanut	Que et al. (2013)

[a] *MWCNT* multi-walled carbon nanotube, *NP* nanoparticle, *AuNPs* gold nanoparticles, *AuNPy* Gold nanopyramides, *GO* graphene oxide, *rGO* reduced graphene oxide, *ErGO* electrochemically reduced graphene oxide, *SWCNT* single-walled carbon nanotube, *Au@AgPt* gold core and silver-platinum shell, *PSA* polystyrene-*co*-acrylic acid, *PANI* polyalanine, *PtNPs* platinum nanoparticles

[b] *Ab* antibody, AFB_1 aflatoxin B_1, *OTA* Ochratoxin A, FB_1 Fumonisin B_1, *DON* Deoxynivalenol, *ZEN* zearalenone, *HRP* horseradish peroxidase, *BoNT/A* Botulinum neurotoxin serotype-A, *BoNT/E* Botulinum neurotoxin type-E, *RαMIgG-ALP* rabbit anti-mouse IgG-alkaline phosphatase, *SEB* Staphylococcus enterotoxin-B, *AChE* acetylcholinesterase, *NOR* norethisterone

3.1 Active Systems for Packaging

Concerning this first category, it is known that most of protective coatings are based on polymeric materials, primarily due to their undeniable chemical stability, mechanical resistance, and minimal (but effective) capability of preventing microbial spoilage. Examples including polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), and other synthetic polymers have been extensively used for this purpose due to their facile production (Nur Hanani 2018). The first advance of going to nanoscale is the reduction of environmental impact associated with the disposability of packaging. Since the high surface-to-volume ratio increases the activity when compared to their macroscopic equivalents, using nanosized polymers would decrease drastically the quantity of material, reducing the amount eventually dumped into the environment, although micro- and nanosized non-biodegradable plastics have arisen as a major concern regarding aqueous ecosystems (Fadare et al. 2020). In this way, an eco-friendlier condition could be achieved using nanostructured biodegradables organic polymers, such as polylactic acid (PLA), poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), and polyvinyl acetate (PVA), as alternative to environment-harmful petroleum-based plastic (Rezaeigolestani et al. 2017; Ding et al. 2017; Li et al. 2019). Thus, great efforts to elaborate synthetic routs have been made to obtain a wide variety of nanostructure forms fog these polymers (Fahmy et al. 2020). At the same time, investigative studies of carbohydrate polymer properties, including starch, cellulose, and chitosan, have been carried out for the development of versatile active coating for food packaging applications (Yang et al. 2018; Lavoine et al. 2016; Abreu et al. 2015). Lavoine et al. found that cellulose nanofibers coatings on paper substrates were able to induce the gradual release of caffeine and chlorhexidine digluconate, which have antioxidant and antimicrobial properties, respectively, that could extend product shelf life (Lavoine et al. 2016). Thanks to the nanoporous network capable to perform reversible interactions with small molecules, cellulose nanofiber is one of the most interesting materials for controlled release of active substances, with the extra advantage of high flexibility and resistance (Almasi et al. 2020). Similarly, polymeric coatings can produce highly active hybrid materials when associated with other nanostructures, acting as appropriate substrate for silver nanoparticles (AgNPs) for example, which are well-known for their excellent antibacterial activity and have been extensively applied in food packaging (Jafarzadeh et al. 2020). Pandey et al. presented a new fibrous hybrid layered chitosan/PVA/AgNPs nanocomposite (nanolayers, NL) prepared by electrospinning technique which has been applied as protective coating for meat packaging. The amount ratio of the constituent materials of the nanolayer was evaluated by testing different proportions in a microbial growth assay, including pure PVA (P-100 NL), 70% PVA, 30% chitosan (P70–CH30 NL), 70% PVA, 30% chitosan + AgNPs (P70–CH30–Ag NL), 60% PVA, 40% chitosan (P60–CH40 NL), 50% PVA, 50% chitosan (P50–CH50 NL), and 100% chitosan (CH–100 NL). The P70–CH30–Ag NL material showed a significantly lower bacterial growth compared to normal plastic packaging in an assay containing *Listeria monocytogenes* and

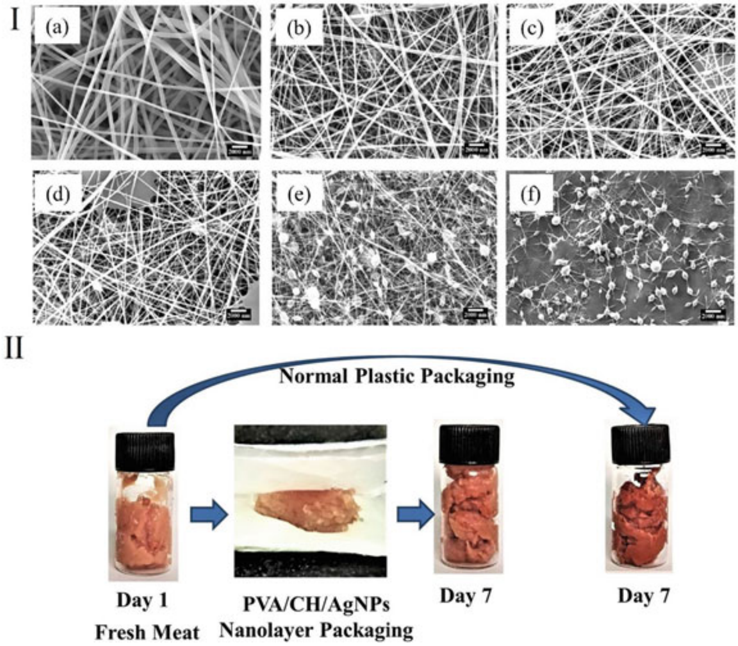

Fig. 3 (**I**) SEM images of electrospun composite nano-layers: (*a*) P-100 NL, (*b*) P70–CH30 NL, (*c*) P70–CH30–Ag NL, (*d*) P60–CH40 NL, (*e*) P50–CH50 NL, (*f*) CH-100 NL. (**II**) Application of PVA/CH/AgNPs composite nano-layer for packaging of fresh meat. (Copyright 2020. Reproduced and adapted with permission from Elsevier B.V. (Pandey et al. 2020)

E. coli (Fig. 3). In addition to the biodegradable polymer matrix, the nanocomposite uses AgNPs from green biosynthesis, which gives a higher added value considering the low impact approach (Pandey et al. 2020).

Based on the presented reasons, the combination of polymeric matrices with antimicrobial agents, antioxidants, absorbers, and many other materials chemical species generates countless possibilities for active coating. The enhanced activity and low impact of these hybrid materials make the use of single material-based functional coating no longer interesting since multi-features packaging.

Alongside AgNPs, other metallic nanoparticles, including gold and copper, have been used as active inorganic material incorporated to packaging to prevent growth of food-borne pathogenic microbes and other multifunctional activities. The mechanism of antimicrobial effect associated with these materials is not well-understood; however, the most accepted hypothesis is the generation of reactive oxygen species (ROS) on the surfaces of nanoparticles, which induce oxidative stress and death of bacteria cells (Jagadish et al. 2018). Jayaramudu et al. proposed a nanocomposite hydrogel containing copper nanoparticles supported in a hydroxypropyl methylcellulose matrix (HCuNPs) as a protective coating tested successfully against *E. coli* and *S. aureus*. The bactericidal was attribute to surface interactions between the composite hydrogel and bacteria via hydroxyl radical generation. As an additional advantage for packaging besides the antimicrobial effect, the presence of HCuNPs improved the material thermal resistance increasing the polymer melting point (Jayaramudu et al. 2021).

Metal oxide nanoparticles such as TiO_2, ZnO, and CuO can perform similar antimicrobial effects, with the additional advantage of being a less expensive alternative to metallic nanoparticles, good U.V. light absorber, and present good resistance to severe conditions of processing steps in food chain (Garcia et al. 2018). In particular, TiO_2 is presented a high abundance compound with long durability, and also presenting an ease for nanosizing, which increases surface–volume ratio and improves photochemical properties; since TiO_2 is excellent U.V. light absorber, it can be used to prevent photodegradation associated with indoor lighting throughout the storage period with the use of mercury lamps, or sporadic sun exposure during transport. Additionally, controlled light irradiation of TiO_2 can promote photochemical reactions to generate high concentration ROS with strong antimicrobial activity. The photoactive chitosan/TiO_2 nanocomposite reported by Zhang et al. showed to be a multi-feature for grapes packaging due to its highly effective microbicide performance against fungi and bacteria contamination under controlled visible light irradiation, and enhanced mechanical and humidity resistances (Zhang et al. 2017).

Multifunctional packaging features of metal oxide-based nanomaterials can be performed by wide variety of operation mechanisms. To illustrate this concept, we can highlight the differential antibacterial activity of ZnO nanoparticles (ZnO NPs), which acts directly on bacterial quorum sensing. Quorum sensing is a chemical communication mechanism based on substance release by bacteria which regulates biofilms growth, being decisive for colony spread and food spoilage. Al-Shabib et al. reported the quorum sensing inhibition and biofilms formation impairment by biosynthetized ZnO NPs over four pathogenic bacteria, acting directly on a wide range of signalizing substances (Al-Shabib et al. 2016). The ZnO NPs/PLA hybrid coating containing plant-based essential oils presented by Heydari-Majd et al. demonstrated enhanced antimicrobial and antioxidant activities capable to double the shelf life period by reducing lipidic peroxidation levels in fish meat samples. Furthermore, the nanocomposite also showed an increased safety level, since it was able to reduce Zn^{2+} ion migration to acceptable concentration values (Heydari-Majd et al. 2019).

In the case of microbial deterioration, it is known that enzymatic reactions of aerobic bacteria are favored by the presence of O_2, mostly due to infiltration into a package entailing biological deteriorations in food. Moreover, food products often present significant sensitivity to long O_2 exposure, leading to fast spoilage due to oxidation. To avoid this condition, consolidated approaches are considered, including the improvement of impermeability, modifying atmosphere packing (MAP), which is based on replacement of gas content for lesser reactive gases, such as N_2. carbon dioxide-based atmosphere also plays an inhibitory activity against a wide range of aerobic microorganisms at moderate levels around 10–20%. Considering this fact, CO_2 emitter can be incorporated inside packaging based on active substances that gradually release the gas, such as carbonate and bicarbonate (Vilela et al. 2018).

More effective approaches are based on attachment of active substances on protective films for packaging, including antioxidant substances and oxygen scavengers are incorporated to. The first type is usually based on substances release, while the oxygen scavenging allows the absorption the undesirable oxygen. The use of this technique usually presents a better reduction of residual oxygen compared to MAP and can avoid unnecessary contact of food with other substances (Dey and Neogi 2019).

For this purpose, iron nanoparticles (FeNPs) are introduced in oxygen capture systems acting by a mechanism based on the redox reaction of FeNPs surfaces at the presence oxygen, producing an oxide layer. Khalaj et al. were able to produce an O_2 scavenger composite material containing FeNPs and montmorillonite (OMMT) supported in a PP matrix. Compared to the pure PP matrix, the presence of FeNPs (0.2% wt.) reduced O_2 and water impermeability by 55% and 77%, respectively. The incorporation of small amounts of nanostructured OMMT (2.0% wt.), a high surface area clay, also increased impermeability associated with the polymer material and inhibited the gas and water vapor diffusion through the packaging, reducing permeability in 22% and 33%, respectively. This phenomenon was attributed to the extending transport pathway and increased tortuosity associated with the nanoclay, which also increased mechanical properties of packaging (Khalaj et al. 2016).

Similar mechanisms are observed using other metal nanoparticles, such as palladium, which have catalytic activity for hydrogen reduction at the presence of oxygen producing water. However, this approach is limited by the low hydrogen concentration allowed in packaging due to its flammability, limiting the amount of oxygen captured by this process and generating undesirable increasing of humidity (Hutter et al. 2016).

Oxygen scavenging can also be achieved using organic nanomaterials, including polymers containing unsaturated hydrocarbon chains, being 1,3-polybutadiene (and its derivates) a prevalent choice, since unsaturated carbon bonds present in the polymeric structure are susceptible to suffer oxidative degradation at the presence of proper catalyst, and eventually combined to other materials to enhance the O_2 scavenging activity. Hybrid nanocomposite is introduced by Parrino and *co*-authors combined polybutadiene, poly(methacryloxypropyl)silsesquioxane, and TiO_2 to generate a protective coating presenting passive and active functionality to O_2 scavenging. As polybutadiene operates via conventional mechanism, the presence of TiO_2 nanoparticles was able to improve O_2 uptake by 70% via photocatalytic process under light irradiation, generating singlet oxygen which was captured by diphenylisobenzofuran embedded within the matrix (Parrino et al. 2021).

In regard to gas-mediated deterioration of food, nanotechnology can also improve solutions related to ethylene elimination. Ethylene is a plant growth-stimulating hormone which plays an essential role in maturation of fruit and vegetables, wherein it is naturally produced, so that long exposure can lead to early rotting process. In this way, food freshness can be extended using ethylene blocker, which can either hold ethylene from the surrounding environment through adsorption process or consume the gas molecule by triggering chemical reactions. The first type can use high surface nanostructured adsorbents, including zeolites, clays, silica, and active carbon materials, while reactive coatings usually incorporate potassium permanganate ($KMnO_4$), which inactivates ethylene by oxidation reaction and producing CO_2 (Gaikwad et al. 2020).

Tas et al. were able to produce a nanocomposite based on polyrthylene and halloysite nanotubes (HNTs), a natural occurrence aluminosilicate nanoclay based on a hollow tubular structure, presenting high adsorptive capacity. The packaging material was tested against the aging of miscellaneous samples, including tomatoes and bananas, presenting a delay in the ripening process. Furthermore, the HNT-based composite presented a supplementary activity toward to oxygen and water vapor blocking, proving to be an excellent gas barrier (Tas et al. 2017). Other multifunctional packaging features can be achieved using the reactive material approach, as illustrated by the work presented by Ebrahimi et al., based on the preparation of a protective film containing nanosilica and nanoclay (Cloisite 15A) impregnated with $KMnO_4$ in a polyolefin elastomer matrix. The material composition was optimized by statistical methodology and resulted in the maximum ethylene absorption of 67% under controlled experimental conditions. The association of $KMnO_4$ and the nanofillers also reduced water permeability, increase mechanical properties and enhanced water impermeability (Ebrahimi et al. 2021).

3.2 *Sensing Systems for Intelligent Packaging*

Rather than increase shelf life, packaging evolved along decades to play direct interaction with consumers, enhancing protection and giving information about nutrition facts, home storage, and how packages should be further disposed of. However, the information contained in conventional packaging are in general previously standardized and do not comprise data about the eventual changes which may happen in the period between the packaging process and the moment when the customers take the product from the shelf, like temperature oscillations, oxygen and humidity exposure, or even the growth of pathogenic microorganisms. In this way, the incorporation of sensing devices to packaging could produce this extra information.

The design of devices which act in sensing systems combined to packaging requires a set of features that make this approach minimally feasible. As discussed in the previous section, the possibility of miniaturization, easy operation, and interpretation is essential to guarantee good communication with costumers. This scenario conveniently leads us once again to colorimetric and electrochemical sensors applied to POC analytical devices. Here, we will discuss some additional aspects of their operation, but also how they can be incorporated as an important component of intelligent sensing mechanisms to ensure food quality.

Biosensors based on bionanomaterials, in a proper miniaturized form, can be coupled to packages to detect foodborne microorganisms or chemical species related to food degradation. Chen et al. used gold nanorods (GNR) to produce multicolor LSPR biosensor to evaluate fish freshness based on hypoxanthine detection, a volatile catabolic substance generated after ATP breakdown in fish muscle during the death and gradually increases levels during spoilage period. The presence of the enzyme xanthine oxidase, present in the biosensor matrix, leads to H_2O_2 generation at the presence of the substrate, which triggers the GNR etching process via Fenton reaction with Fe^{2+}, producing intermediary gold nanostructures with different colors until total etching at high levels of hypoxanthine (Chen et al. 2017). The colorimetric indicative allows simple differentiation of freshness status and can be easily attached to packaging.

For this simplicity, many LSPR-based colorimetric devices have been developed with the same purpose (Lin et al. 2018; Ma et al. 2017; Bumbudsanpharoke and Ko 2019; Zhai et al. 2019). Hydrogen sulfide (H_2S) is a final product of some microbiotic metabolisms, so that food-released H_2S by food can be an indicative of pathogen bacteria. To detect this chemical species, Koskela et al. reported an Au/AgI dimeric nanoparticles generated by modification of Au@Ag core–shell nanoparticles were used to detect H_2S by alteration in plasmonic oscillations mediated by anionic changes on nanoparticle shell from AgI to Ag_2S, which leads to a visual color change from red to blue. This colorimetric sensor has the require features for ease attachment on packaging to notify the conditions related to of raw food freshness (Zeng et al. 2018).

With respect to physicochemical parameters, temperature monitoring is certainly decisive to ensure quality and safety of food during the storage and transport steps, especially when certain products require low-temperature maintenance, including, fruits, vegetables, meat, milk, and cold beverages. Despite continuous temperature control is part of routine process in food industry, the conditions inside the packaging can be changed by different causes until reach consumers. In order to build a register of temperature variations and deliver this information directly to consumers, miniaturized colorimetric sensors are certainly the best choice to accomplish this task.

In this way, devices known as time and temperature indications (TTIs) are already commercially available. They use irreversible temperature-mediated physicochemical process to provide a color change signal and record a thermal history. Signal generation mechanism generally used in these devices includes use of molecular thermochromic dyes, heat-stimulated polymerization, and enzymatic hydrolysis, so that all of these systems can be nanosized to enhance efficiency. Moreover, intrinsic features of metal nanoparticles like plasmonic oscillations can be managed to generate robust LSPR-based colorimetric temperature sensors (Mustafa and Andreescu 2020).

Zheng et al. presented proof-of principle of a colorimetric TTI device with color change mechanism based on the epitaxial reduction of silver ions on gold nanorods surface at the presence of ascorbic acid as reducing agent. The resulting induction of core–shell configuration of nanorods is triggered with the by the rise of temperature to 30 and 40 °C, indicating the break of the cold chain and presenting a time-dependent change in LSPR maximum absorption spectrum from 880 nm to 690 nm

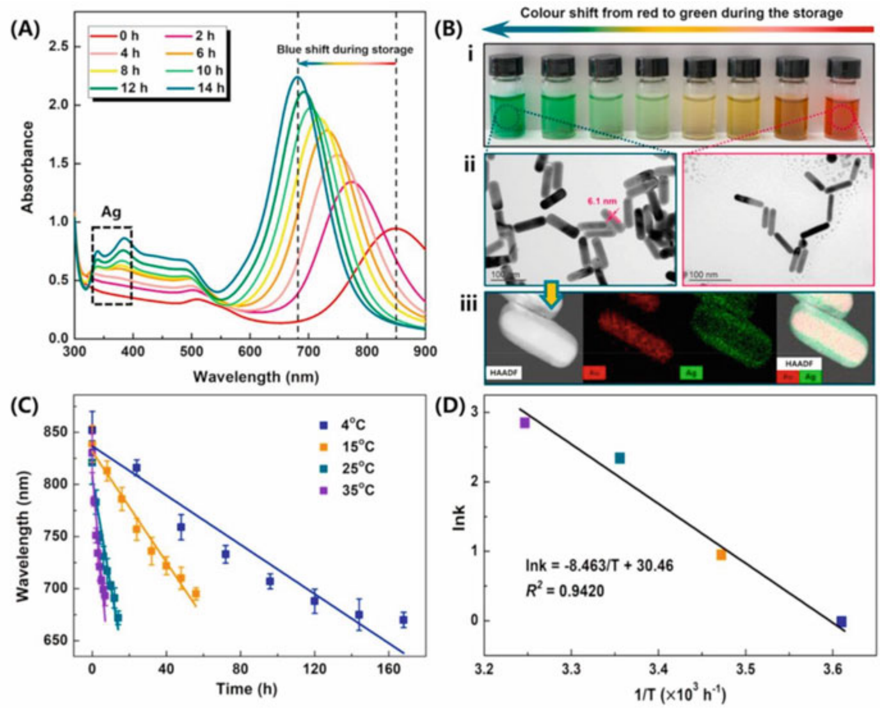

Fig. 4 Characterization, kinetic modeling and E_a determination of the TTI. (**a**) Typical UV–Vis spectra of the TTI with 25 °C as an example. (**b**) Color variations, (*i*) TEM (*ii*) and HAADF–STEM–EDS images (*iii*) of the Au@Ag NRs. (**c**) Kinetic modeling under different temperatures. (**d**) E_a determination based on k values. (Copyright 2021. Reproduced with permission from Elsevier B.V. Gao et al. 2021)

as the thickness of silver shell increases, which is visually detected by a red-to-green change, so that intermediary colors (orange, yellow, and greenish-yellow) could be used to pinpoint more precisely the exposure time (Zhang et al. 2013). A similar thermochromic nanomaterial was used by Gao et al. to obtain a more reliable and intelligent informative label (Fig. 4) and to monitor temperature abuse in pasteurized milk samples with an additional study to statistically correlate the color change indications with milk quality attributes in different storage conditions, including acidity, pH, presence of bacteria, and activation energy (E_a) as indicative parameter of temperature dependence of reaction rate through Arrhenius equation (Gao et al. 2021).

Abuse in frozen temperatures can also promote change in food quality and this condition can be detected and registered using the LSPR approach as well. Mohan and coworkers demonstrated in two works the potential of chitosan-capped gold nanoparticles (CTS–AuNPs) to suffer irreversible processes of aggregation, growth and agglomeration, producing pink to dark gray color variation, under very low temperatures. This highly stabilized nanomaterial remains dispersed under a wide temperature range, so that its aggregation is trigged at temperatures of −20 °C being dependent on the time of exposure. The frozen-mediated color change process was attributed to crystallization of water and following precipitation of CTS, leading to the loss of stabilization of AuNPs and consequent aggregation and agglomeration. The colorimetric indicative of temperature abuse remained even after subsequent replacement of samples to a refrigerator or to a 40 °C room (Wang et al. 2018b; Mohan et al. 2019).

A more creative mechanism with lower risk of substance migration to food is the use of polymeric materials that change light interactions irreversibly according to temperature, as illustrated by the work of Choi et al. which reports the fabrication of a self-healing nanofibers composed of aromatic disulfide-based thermoplastic polyurethane (TPU) and disposed in a map through electrospinning technique. The nanofiber induces visible light scattering at freezer and refrigerator temperature (−20 °C and 2 °C, respectively), generating a white opaque configuration. When temperature rises to room temperature, the nanomaterial gradually increases its transmittance irreversibly, turning transparent over the time range from 0.5 to 22.5 h, being able to reveal a hitherto hidden warning sign "!". Additionally, the material is potentially versatile to detect break of the cold chain in varied time-scales, since the thermo-optic transition of the nanofiber can be tunable according with product storage requirements by changing the composition and thickness of the polymeric film (Choi et al. 2020).

The development of temperature indicator with reversible activity has also demonstrated great importance and good applicability, especially for ready-to-eat food situations, in order to indicate if food products are in the best condition for immediate consume, including beverages like beers and wines that are usually served from refrigerators at low temperature, but eventually stored at room temperatures. An example of a device with such features is the wide temperature range reversible thermochromic nanocomposite presented by Phonchai et al., which used ZnO nanoparticles electrostatically modified with polydiacetylene (PDA) through carboxylate headgroup/Zn^{2+} pairing. The color change of the nanocomposite from blue to purple as the temperature increases is associated with conformational changes on backbone structure of the conjugated polymer, leading to visually readable temperature range from 10 to 90 °C (Phonchai et al. 2019).

Another essential requirement to keep food quality and preservations during storage is humidity control and monitoring, since uncontrolled moisture levels can significantly affect food texture and induce microbial spoilage inside packaging. For humidity detection, we can highlight the application of capacitive sensors which use unique features of inkjet-printed nanomaterials to produce flexible and miniaturized devices, very compatible to the usage as an active tag on different substrates for packaging. Here, we will demonstrate the applicability of this type of sensor coupled to radio frequency identification (RFID) tags, where the signal generation of these devices is usually based on changes in the dielectric constant at the presence of water, which can be remotely processed by portable devices, including smartphones via "internet of things technology" (Singh et al. 2017b; Tsai et al. 2020). Of course, RFID tags also can be incorporated to the variety of sensors previously reported, but due to the prominent number of publications relating this technology to humidity sensors, they will be the main focus here.

The incorporation of nanomaterials usually is associated with two basic components of RFID devices: a sensing film or electrode responsible to transduce the analytical signal related do humidity, and the RFID antenna, responsible for capturing the radiofrequency signal. A combination of the use of a graphene oxide (GO)-sensing film layered on a graphene antenna printed on a paper substrate was presented by Huang et al. to generate a battery-free humidity sensor capable to operate at GHz frequencies. GO presents relatively high hydrophilicity thanks to hydroxyl and epoxy groups dispersed on structure of the material. For this reason, GO can retain large amount of water from the surrounding environment, increasing its dielectric permittivity, which was used to correlate to relative humidity (RH) varying from 10 to 100% (Huang et al. 2018).

RFIT tag sensors are compatible to a large variety of nanomaterials and the inkjet printing technology allows the attachment of tags on and also large variety of substrates, producing flexible and wearable devices. A versatile approach with promising results using different materials can be illustrated by the low-cost humidity sensor proposed by Aziz et al. based on screen-printed electrodes structured via a nanocomposite ink, containing poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and $ZnSnO_3$ nanocubes, fabricated using a water assisted transfer technique capable to transfer the design to substrates with varied forms, including flat and curved ones, which is certainly suitable for application in packaging. The device was able to measure RH levels via impedance response from 0 to 90% (Aziz et al. 2016).

4 Environment, Health, and Safety

One of the greatest purposes of the inclusion of nanomaterials in food is to enhance health and to guarantee safety of consumers against pathogens and contaminations. Antibacterial nanoparticles, nanocapsules for nutrient delivery, and the nanomaterials present in sensors attached to intelligent packaging share all the same goal. However, questions about how the presence of these extremely small materials affects consumers and food industry workers have constantly arisen, as well as if there are potential risks associated to environment contamination. As a developing technology, the data about food nanomaterials impact on the environment and human health is limited, which may difficult the advancement and incorporation of regulatory measures and safety policies once these discussions arise as these new materials and devices are created. Moreover, the discussions go beyond the academic media, since the expanding food trade at global level has resulted in the increase of consumer concerns, not only about food quality, but also about their confidence in the new materials that come with food products. Here, we will discuss aspects of potential risks associated with nanoencapsulation systems in food, migration of nanomaterials contained in packages, and potential ecotoxicity.

Nanotechnology provides a series of benefits associated with food quality, including protection against pathogenic microorganism and enhancement of nutritional value via nanoencapsulation. However, it is not clear how nanomaterials can interact with food components or gastrointestinal tract causing adverse physiological responses. Ideally, the ingestion of nanomaterial should interact with gastrointestinal tract through three different ways: (1) being fully digested and absorbed, including stabilizing agents, such as surfactants; (2) partially or not digested with the non-digestible component being promptly excreted; and (3) nanomaterials resistant to gastric digestion, if not excreted and absorbed through intestine epithelium should not induce immunological and toxicological damage (Jafari et al. 2017). However, ideal situations may not be applicable for all materials incorporated to food. A elucidated example is associated with SiO_2 nanoparticles, used as anti-caking agent, which can interact with food, leading to gastrointestinal adverse effects and disturb nutrient absorption (Go et al. 2017).

Potential risks associated with the migration of nanomaterials from packaging to food can negatively affect the market. The use of AgNPs and other antimicrobial agents in packaging, for example, is a well-established technology. However, there are concerns about the risks associated with the eventual ingestion of AgNPs and Ag^+ ions migrated from protective coating to food and beverages, especially with the possibility of bioaccumulation of AgNPs in vital organs, such kidneys, brain, and liver (Gallocchio et al. 2016). Moreover, the eventual ingestion of microbicide materials may cause damage to both pathogenic and beneficial gut bacteria, affecting the gastrointestinal tract (Siemer et al. 2018; McClements and Xiao 2017).

Multifunctional metal oxide-based nanocomposites, such as TiO_2 and ZnO, are also extensively used for packaging applications, but human exposure to these compounds is not yet well-elucidated and may lead to cytotoxic and genotoxic conditions. In vitro studies showed that TIO_2 nanoparticles can induce toxicological effects by inhibition of expression of important regulators related to cell cycles (Montalvo-Quiros and Luque-Garcia 2019). Similarly, ZnO also can present toxic effects in human body, either in solid nanoparticle form or in solubilized Zn^{2+}. Direct inhalation of ZnO nanoparticles (ZnO NPs) can result in lung inflammation and systemic toxicity and the inherent generation of ROS may lead to of inflammatory response, as well as to neurotoxic effects, since ZnO NPs can pass through the blood–brain barrier. Furthermore, the aggregation of particles inside the cells or Zn^{2+} intake can cause DNA damage (Singh 2019; Sruthi et al. 2018).

Of course, the low concentrations of these materials found in packaging are not considered to be harm to customers and, in adequation conditions, could be negligible, since the most studies involving noncompounds migration reported contamination levels lower than standard limits established by regulatory organs (Emamhadi et al. 2020). However, as customer's exposure studies are difficult to perform, there is no evidence indicating that long-term exposure to nanoparticles in food products is safe. More than create nanocomposite films with high efficiency and low probability of substance transferring to food, security studies concerning substance migration should be considered in the development of new packaging technologies as well. In fact, attempts to development of migration test have been carried out in several food matrices. However, several factors may affect the results of such studies, experimental conditions are not yet standardized, and they should simulate as close as possible the real-life scenarios related to customers interactions with food. Additionally, there is a major concern about worker of food industry who are direct exposed to large amounts of these materials. Despite the advanced strategies to measure and minimize workplace exposure, the lack of regulation makes difficult the suitability and improvement of these approaches (Kuhlbusch et al. 2018).

Along with human health, concerns about impact of nano-based packaging and nanowaste in the environment are also a major issue. Understanding the real ecotoxicological effects of the release of these substances in aquatic environment, soil, and trophic levels is crucial to guarantee the application of initiatives no mitigate the impact. However, due to the extremely small sizes and low concentrations of these materials and high reactivity with the possibility of structural changes as they travel through the environment, it is required highly sensitive analytical methodologies which can achieve low limits of detection and specific identification, and even then, it would be difficult to trace the source of the contamination (Mazari et al. 2021).

As the mechanisms of interactions of nanomaterials with environment are elucidate, initiatives can be taken in the early design and production of nano-based packaging. Indeed, the introduction of intelligent packaging with proper instructions and procedures for disposal could help to reduce nanowaste and the related environment issues. Furthermore, the use of biodegradable polymers and the development of green routes for nanoparticles synthesis (bio-synthesis) to produce eco-friendly products may minimize the indirect environmental impact, but not sufficiently (Kuswandi 2017).

Among all concerns that need to be addressed for the use nanomaterials, governmental agencies regulation initiatives around the globe would have a key role and major impact in health and environment issues. However, the advancement of these initiatives around the world still walk slowly. Only United Kingdom, Switzerland, and European Union have already advanced on the development of legislations with specificity for nanomaterials and have been incorporated in legislation for agriculture and food production, including information requirements for potential risks related to nanomaterials exposure (Amenta et al. 2015). In United States, Food and Drug Administration (FDA), despite being a precursor in the definition of nanotechnology, has not yet adopted a regulatory definition of nanomaterials, but have worked to develop and provide the necessary information to achieve proper regulation and introduced specific guidance documentation for nanotechnology use in food production directed to manufacturers, which includes safety alerts (FDA 2014). While in Latin America developing countries, including Brazil, Mexico, and Argentina, have introduced efforts to improve research in nanotechnology, including new funding and government initiatives, but still struggle in including regulation with specific criteria, especially for environmental impact (Ponce et al. 2018).

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Nanotechnological Achievements and the Environmental Degradation

Shimaa M. Ali and Khadija M. Emran

1 Introduction

The removal of organic pollutants is mandatory, since above its highest allowed critical concentrations, it is harmful to humans and aquatic lives. A possible way to eliminate pollution is by using nanotechnology, by which it is possible to control shape and/or size of nanoparticles, and therefore, optimize its performance for pollution removal. Nanomaterials can be used for the removal of pollutants and treatment of wastewater through different removal mechanisms (Mehndiratta et al. 2013). The most common removal mechanisms are photocatalytic and chemical, electrocatalytic degradation, Fenton reaction, and adsorption.

1.1 Photocatalytic Degradation

Semiconductor-based heterogeneous photocatalysis can be used for the degradation of various organic pollutants in wastewater, such as dyes, pesticides, and other organics. As it contributes efficiently in an advanced oxidation process, which is strongly correlated to the degradation of organic pollutants. The photo-excited TiO_2 has strong redox properties especially when its crystal size is reduced to the nanodimension. The strong photocatalytic activity is related to its wide bandgap;

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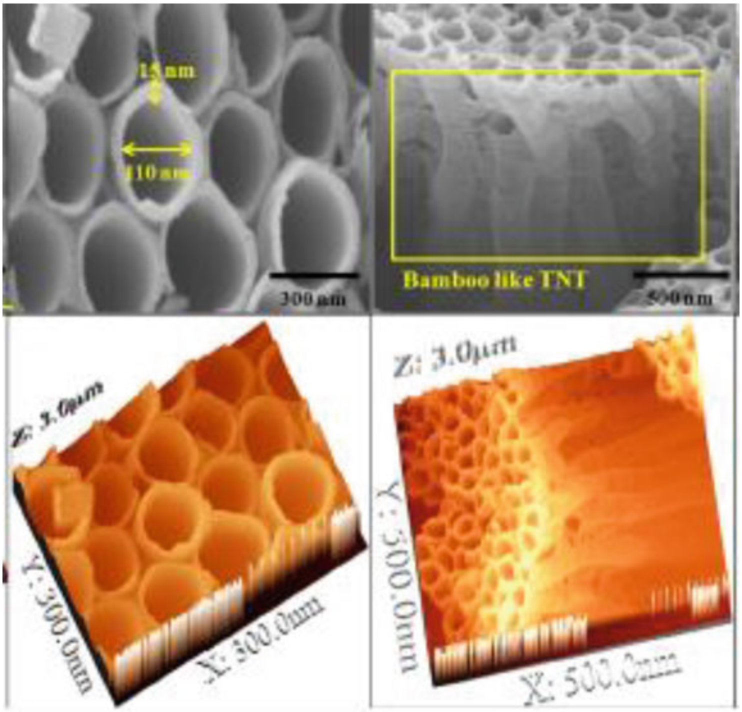


Fig. 1 FESEM and AFM images of titanium/niobium oxide nanocomposite (Indira et al. 2021)

in addition, it is nontoxic and offers a good stability in water (Fujishima and Honda 1972). However, TiO_2 suffers from some limitations, first, its excitation is dependent on the UV light, which constitutes less than 5% of the sun power. Second, it produces a huge electron–hole pairs upon excitation, which negatively affects the efficiency of the photocatalyst (Li et al. 2005; Kubacka et al. 2008). For these reasons, recent researches focus on the use of TiO_2 photocatalyst with minimizing its disadvantages through doping concept or composite formation.

Ceria-based TiO_2 nanomaterials were successively used in the photocatalytic degradation of organic dyes. CeO_2 has a suitable bandgap size and can be used to store or release oxygen easily due to the well-known Ce^{3+}/Ce^{4+} redox shift, which, in turn, prevents the electron–hole pairs recombination. CeO_2-doped TiO_2 nanocrystals, synthesized hydrothermally, have been used for the photo-catalytic degradation of rhodamine B (RhB) dye using UV and UV/visible light for 8 h, where 99.89% of the dye was degraded (Kasinathan et al. 2016). CeO_2/TiO_2 composite offers higher surface area and redox activity than the parent single oxides, prepared by the same method. Bamboo-like nanotube arrays with open top structure of titanium/niobium oxide nanocomposite were prepared by first anodization, and then, niobium ions were incorporated via the dip coating (Indira et al. 2021), as shown in Fig. 1.

The degradation mechanism of organic pollutants by the photocatalyst $TiNb_2O_7$ nanocomposite can be due to the oxygen radicals formed by the reduction of oxygen in the conduction band by the photo-generated electrons, and the hydroxyl radicals resulted from the reaction of holes with adsorbed water in the valence band. These radicals can strongly degrade the organic pollutants into nonharmful carbon dioxide and water. A series of Sn-doped TiO_2, $Sn_xTi_{(1-x)}O_2$, photocatalyst with SiO_2 as a supporting material was employed for the degradation of RhB under UV light (Khandekar et al. 2019). Impregnation of the photocatalyst within the silica pores was confirmed and reduced crystal size and bandgap for Sn-doped titania were observed compared to those of the undoped one. In addition, the doping of TiO_2 with Sn enhanced the photocatalytic activity. $Sn_{0.05}Ti_{0.95}O_2/SiO_2$ showed the highest pseudo-first-order degradation rate constant of 1.36 h^{-1} for RhB dye, at pH 4.5. $SrTiO_3/TiO_2$ nanocomposite, supported on activated carbon, was examined as a photocatalyst for the degradation of 2,4-dichlorophenol and bisphenol A, and compared to commercial P25 TiO_2 (Ali et al. 2019). $SrTiO_3$ is a well-known p-type perovskite-type oxide, and it can form a heterojunction with n-type TiO_2 oxide, which facilities a charge separation of photogenerated electron–hole pairs and prevents its recombination. Nano-TiO_2@polyfluorene composite was prepared through the solid-state oxidative coupling reaction of fluorene with $FeCl_3$ and tetrabutyl titanate (Bai et al. 2020). Conjugated polymers can enhance the photocatalytic activity due to its high quantum efficiency. An excellent photocatalytic activity of the prepared composite for the degradation of malachite green and RhB is observed under sunlight or under visible light. In case of UV-irradiation, polyfluorene can be excited. The photoelectrons generated at the lowest unoccupied molecular orbital level of the excited polyfluorene can transfer to the lower conduction band of the excited TiO_2. Therefore, electron–hole pairs can be easily transferred to TiO_2, and the rate of active species production is increased on the composite surface, as shown in Fig. 2. Under visible light irradiation, the mechanism is different, because large bandgap TiO_2 cannot be excited. Only polyfluorene can be excited resulting in the formation of electron–hole pairs. Active species arose from the transfer of photoelectrons from the lowest unoccupied molecular orbital level of polyfluorene to the lower valence band of TiO_2.

Chemically synthesized nano-CaO particles, prepared from waste eggshell, can be used as photocatalyst in degradation of organic dyes (Sree et al. 2020). CaO is an effective photocatalyst for dyes degradation, where most of methylene blue is degraded in 15 min, while toluidine blue is degraded in 10 min. The study of scavenger showed that the oxygen has an important role in the photocatalysis. The use of citric acid as a cross linker resulted in a more efficient chitosan–CaO beads than the use of glycerol. However, the free chitosan–CaO beads has a higher efficiency. The catalyst recycled for seven cycles, the dye degradation efficiency was decreased due to the catalyst loss by leaching and pores blocking as indicated in Table 1.

Due to its narrow bandgap, 1.2–1.9 eV, CuO, a p-type semiconductor, have a photocatalytic activity under visible light. The visible light photocatalytic activity of 1D copper oxide nanorods, prepared by the thermal oxidation of Cu wires, is tested

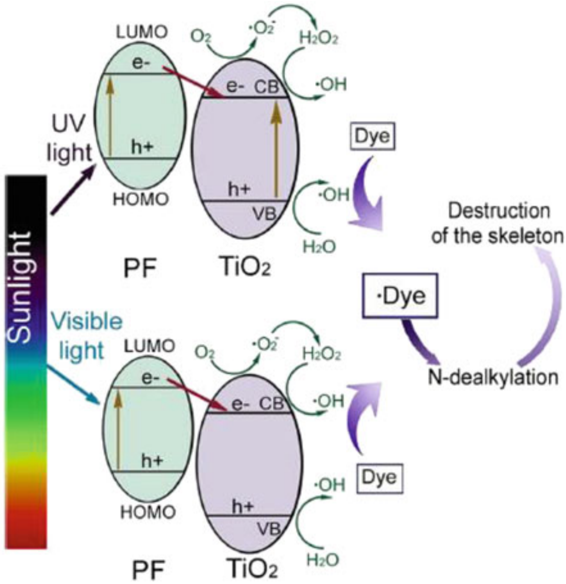


Fig. 2 Photocatalytic activity mechanism in the TiO_2@polyfluorene composite particles under both UV and visible light irradiation (Bai et al. 2020)

Table 1 Percentage of reduction of reused catalyst in each reaction (Sree et al. 2020)

Number of cycles	Degradation efficiency	Efficiency reduction %
1	96.19	0
2	92.43	3.90893
3	89.52	6.934193
4	86.45	10.12579
5	83.29	13.41096
6	79.31	17.5486
7	76.58	20.38673

using the degradation of methyl orange reaction (Kottappara et al. 2021). Photodegradation performance of the hollow CuO nanorods is better than those for reported CuO and its nanocomposite in the literature. It was found that the synthesis of CuO nanoparticles at different annealing temperatures resulted in different morphological nanostructures which in turn showed different photocatalytic performance. Hollow morphology of CuO has an improved photocatalytic degradation activity due to spaces arised from the pores formation in hollow CuO nanowires. The photodegradation characteristic of a series of a mixed oxides ZnO/CuO nanocomposites with different metals molar ratio, prepared via low-temperature hydrothermal synthesis, was investigated (Kumari et al. 2020a).

By the incorporation of CuO into ZnO, the rate of the charge carriers recombination is decreased, and the rate of photogeneration of charge carriers is increased, resulting in an improved optical activity. An additional reason is the affected morphology of ZnO-by-CuO nanoparticles, where the latter increased the amount

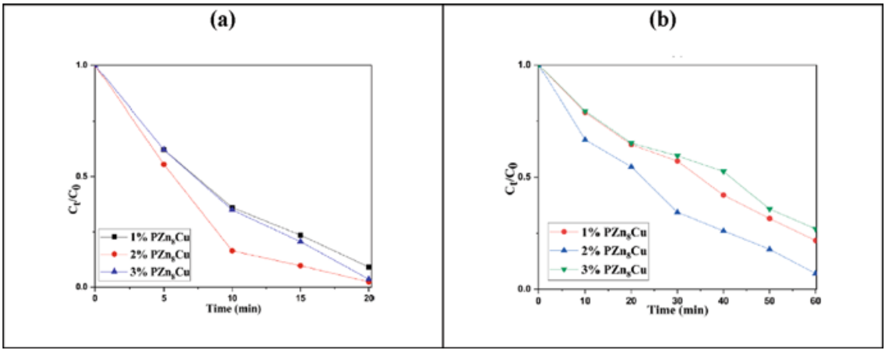


Fig. 3 Photodegradation of pollutants using synthesized materials RhB (**a**) and triclopyr (**b**) (Kumari et al. 2020b)

of the photogenerated holes. In this case, holes are the most active species for the photocatalytic deterioration of RhB as compared to other species, such as superoxide hydroxyl radicals. The degradation efficiency of Pd-deposited ZnO/CuO (8:1) nanocomposites for two organic pollutants, RhB and triclopyr, was evaluated (Kumari et al. 2020b). An enhanced photodegradation efficiency resulted by the use of an optimized amount of Pd, 2%, as shown in Fig. 3. The presence of Pd allowed the absorption to shifts to near IR region and, therefore, reduced the rate of charge carriers recombination.

The degradation of reactive violet 5 by a photocatalytic treatment with Fe-doped TiO_2 photocatalysts exposed to visible light was performed (Zuorro et al. 2019). P-25 TiO_2 and three Fe levels: 10Fe–TiO_2, 50Fe–TiO_2, and 100Fe–TiO_2 were tested. The removal of efficiencies was found about 23% (P-25) to 47.6% (50Fe–TiO_2). The photocatalytic treatment of reactive violet 5 by the 50Fe–TiO_2 catalyst was effective not only for color removal, but also for the degradation of the aromatic structures of the dye molecule and its cleavage into smaller fragments. According to the experimental data of photocatalytic dye degradation, the optimal pH was equal to 10. The influence of this pH on dye removal was attributed to its effects on the generation of radical species hydroxyl radicals ($^{\cdot}OH$) at the catalyst surface during the photocatalytic process from the oxidation of OH^- or H_2O and breaking the –N=N– bonds and causing decolorization of the dye solution.

MnO_2 nanoneedles, with a length of 200–400 nm distributed uniformly on the graphene oxide nanosheets, have been prepared through a low-temperature reflux condensation method. The presence of graphene oxide in the nanocomposite resulted in a larger surface area than MnO_2 nanoneedles, and increased number of surface oxygen containing functional groups, which suggest its possible use for the degradation of the norfloxacin via peroxymonosulfate oxidation (Wu et al. 2020). MnO_2/graphene nanocomposit can be more efficiently coupled with peroxymonosulfate for norfloxacin removal than MnO_2 nanoneedles. It, therefore, exhibited a better degradation performance at a larger pH range and a higher stability. In a similar mechanism, MnO_2/graphene oxide nanohybrids can be used for the degradation other fluoroquinolone antibiotics, such as ciprofloxacin and enrofloxacin and, consequently, for the removal of antibiotics in the environment.

The ability of polydimethylsiloxane (PDMS)−TiO_2−gold (Au) composite sponge as plasmonic photocatalysts to decompose the organic pollutant RhB in water was tested under UV and visible light (Lee et al. 2020). Comparison with PDMS−Au, PDMS−TiO_2 sponge shows more photocatalytic. For PDMS−TiO_2 sponge, The dye concentration significantly decreased under UV light, and was near constant under dark and visible light. Where PDMS−Au sponge shows RhB decomposed even in dark conditions, although this was significantly slower than under light. This can be attributed to the catalytic, not photocatalytic, activity of the Au NPs. The performance of PDMS−TiO_2 is consistent with the photocatalytic property of TiO_2 for UV light, according to follow reactions:

$$TiO_2 + hv\,(UV) \rightarrow TiO_2{}^*(e_{CB}{}^- + h_{VB}{}^+)$$
$$H_2O + h_{VB} \rightarrow OH^{\cdot} + H^+$$
$$O_{had}{}^- + h_{VB} \rightarrow OH_{ad}{}^{\cdot}$$
$$e_{CB} + O_2 \rightarrow O_2{}^{\cdot -}$$
$$\text{Rhodamine B} + (OH^{\cdot}, OH_{ad}{}^{\cdot}, O^{\cdot -}, \text{ or } h_{VB}{}^+) \rightarrow \text{photodegraded intermediates} \rightarrow H_2O + CO_2$$

($TiO_2{}^*$ is the excited state of TiO_2, $e_{CB}{}^-$ is a photoexcited electron in the conduction band, $h_{VB}{}^+$ is a photogenerated hole in the valence band, $OH^{\cdot}$ is a hydroxyl radical, $OH_{ad}{}^-$ is an adsorbed hydroxide ion, and $O_2{}^{\cdot -}$ is a superoxide). For the PDMS−TiO_2−Au sponge, under UV light, it showed 1.8 times faster RhB decomposition rate than the PDMS−TiO_2 sponge, and 7.4 times faster rate than the PDMS−Au sponge. This confirms a synergistic effect between TiO_2 and Au NPs for photocatalysis.

Polyaniline−TiO_2-based photocatalysts for methylene blue and RhB dyes degradation (Jangid et al. 2021). According to the results, the photocatalytic activity of the PANI/TiO_2 nanocomposites is developed by the deposition of PANI on TiO_2 nanoparticles, as shown in Fig. 4 (PANI nanowire grown on TiO_2 nano/microfiber).

The pristine TiO_2 nanoparticles revealed 89% degradation of dye, while 93% of degradation was observed by the PANI/TiO_2 nanocomposite. The reason behind the enhancement was the specific surface area, large interaction between composite photocatalyst, and also results in a decrease of the aggregation in the nanocomposite. The decolorization efficiency of photocatalytic degradation of methylene blue 98.6% is compared to 76.7% for PANI nanotubes when PANI/TiO_2 composite nanotubes were used as the catalyst (Jangid et al. 2021).

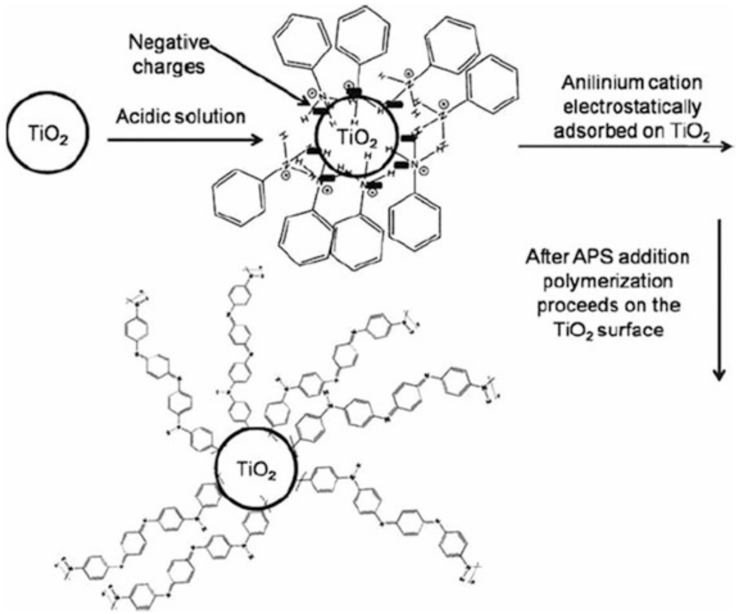


Fig. 4 Formation scheme of PANI/TiO_2 core–shell nanocomposite (Jangid et al. 2021)

1.2 Chemical Catalytic Degradation

Advanced oxidation process can be widely applied for the environment decontamination via pollutants oxidation, as it is effective, easy technology. Hydroxyl radicals ($^{\cdot}OH$), produced in homogeneous oxidation reactions, can be used to degrade many types of organic pollutants quickly and nonselectively. In this type of degradation, the oxidative activity of the nanomaterials is investigated by degrading the organic pollutant in water without light irradiation, at a given pH and temperature. The degree of exposure of crystal facets is strongly affecting the reactivity of oxidizing materials. δ-MnO_2 was prepared, with different exposure facets, and applied as oxidants, without light irradiation, for the degradation of phenol from aqueous solutions (Pham et al. 2020). $\delta - MnO_2 - \{-111\}$ showed a higher degradation rate of phenol and many other organic pollutants, such as ciprofloxacin, bisphenol A, 3-chlorophenol, and sulfadiazine than $\delta - MnO_2 - \{001\}$. The $\{-111\}$ facet exhibited a better oxidation character for the pollutants degradation due to its high density of Mn^{3+}. Moreover, the formation of the superoxide radicals ($O_2^{\cdot -}$) is promoted in the case of the $\{-111\}$ facet due to the adsorption/activation of oxygen. $O_2^{\cdot -}$ radicals can be strongly contribute to the oxidative pollutants degradation. Degradation of methylene blue dye by β-MnO_2 nanoparticles was examined in the presence of hydrogen peroxide (H_2O_2) and radical scavengers (Wang et al. 2021a). Nano-sized β-MnO_2 can be used effectively for the dye degradation due to the catalytic oxidation of H_2O_2 on β-MnO_2 surface reactive sites, rather than the adsorption. The methylene blue degradation rate was decreased in the presence of p-quinone and sodium azide, indicating the important role of the singlet oxygen radical ($^1O_2$). First, H_2O_2 was rapidly absorbed and then decomposed on the catalyst surfaces. Then, the $^1O_2$ radicals are formed, and used with the $O_2^{\cdot -}$ radicles for the oxidation of methylene blue. Next, the residual H_2O_2 slowly decomposed to generate free radicals, which degraded methylene blue more efficiently. Besides, $^1O_2$ radical can also produce from the oxygen dissolution (Eqs. 1–4), and this proves that $^1O_2$ can be formed by the reaction of β-MnO_2 with oxygen. Furthermore, the superoxide anion generated by the MnO_2/H_2O_2 system could enhance the oxygen formation (Eqs. 5–8), which strongly accelerate $^1O_2$ radicals formation. Therefore, circular interactions between β-MnO_2 and H_2O_2 to form radicals and then oxidize methylene blue can be proposed:

$$Mn^{3+}/Mn^{4+} + H_2O_2 \rightarrow Mn^{2}/Mn^{3+} + O_2^{\cdot -} + 2H^+ \tag{1}$$

$$O_2^{\cdot -} + H_2O \rightarrow \cdot OH + H_2O_2 \tag{2}$$

$$Mn^{2+}/Mn^{3+} + O_2 \rightarrow Mn^{3+}/Mn^{4+} + H_2O_2 \tag{3}$$

$$Mn^{3+}/Mn^{4+} + O_2 \rightarrow Mn^{2+}/Mn^{3+} + {}^1O_2 \tag{4}$$

$$[\equiv M - O]OH - H_2O_2 \leftrightarrow [\equiv M - O] + \cdot OOH + H_2O \tag{5}$$

$$[\equiv M - O] + \bullet OOH \rightarrow [\equiv M - O]H + O_2(g) \uparrow \tag{6}$$

$$H_2O_2 + \bullet OOH_2 \rightarrow O_2^{\bullet -} + H_2O + OH^- \tag{7}$$

$$\bullet OOH + O_2^{\cdot -} \rightarrow HOO^- + O_2(g) \uparrow \tag{8}$$

Nanomagnetite (nano-Fe_3O_4) can be used for the oxidative degradation of tetrachloroethene in the presence of glutathione as a catalyst (Mohamad et al. 2020). It was found that a complete degradation of tetrachloroethene in the nano-Fe_3O_4–glutathione suspension can be achieved at pH 7 in 4 h. The rate constant for the oxidative degradation of tetrachloroethene in the nano-Fe_3O_4–glutathione suspension was 11.7 times faster than that in the nano-Fe_3O_4 suspension (Fig. 5). Glutathione acts as a reductant to convert Fe^{3+} to Fe^{2+} and facilitates the formation of active oxygen species used for the oxidative degradation of tetrachloroethene by nano-Fe_3O_4. The oxidation of tetrachloroethene resulted in oxalic acid via hydroxylation, as shown in Fig. 6.

The recyclable magnetic C/nano-Fe_3O_4 composite adsorbent was successfully used for the removal of trichloropropyl phosphate from aqueous solutions (Wang et al. 2021b). The optimum mass ratio of C to nano-Fe_3O_4 is 1:5, where it exhibited the highest performance with an easy separation. Higher ratios resulted in low adsorption efficiencies and lower ratios weakened the ability of magnetic separation of C/nano-Fe_3O_4 composite from water. At optimum ratio, a maximum adsorption capacity of C/nano-Fe_3O_4 composite for trichloropropyl phosphate was obtained, 2682.1 μg/g. Kinetics studies showed that the equilibrium can be achieved within 3 h. Trichloropropyl phosphate can be removed within 3 h in the Fenton-like system

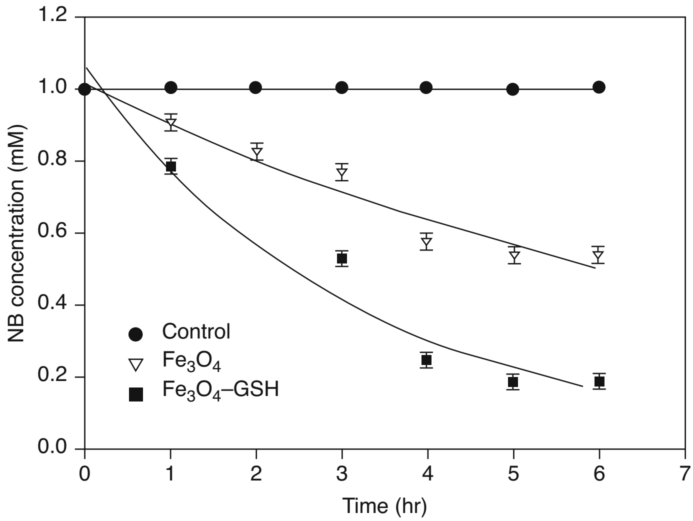
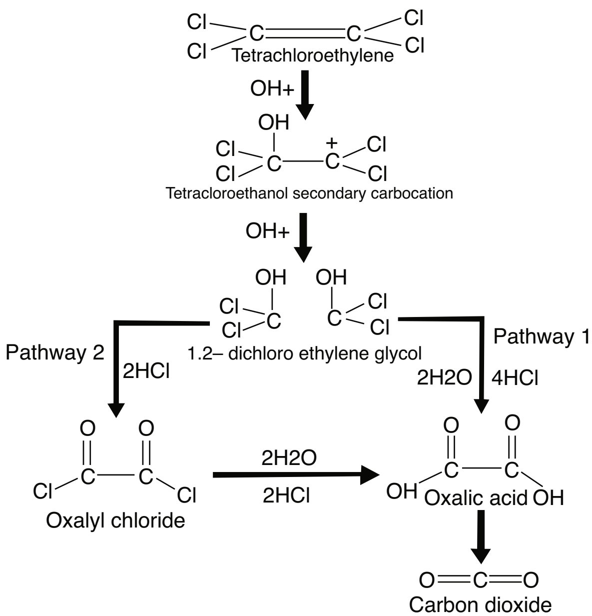


Fig. 5 Oxidative transformation of tetrachloroethene by nano-nano-Fe_3O_4–glutathione suspension (Mohamad et al. 2020)

Fig. 6 Degradation mechanism for oxidative degradation of tetrachloroethene by nano-nano-Fe_3O_4–glutathione suspension (Mohamad et al. 2020)



and within 8 h in the activation system. The trichloropropyl phosphate degradation in the Fenton-like system is favored at low solution pH, while high solution pH was more suitable for efficient trichloropropyl phosphate degradation in the activation system. A proposed mechanism showed that the preferred attack points are three

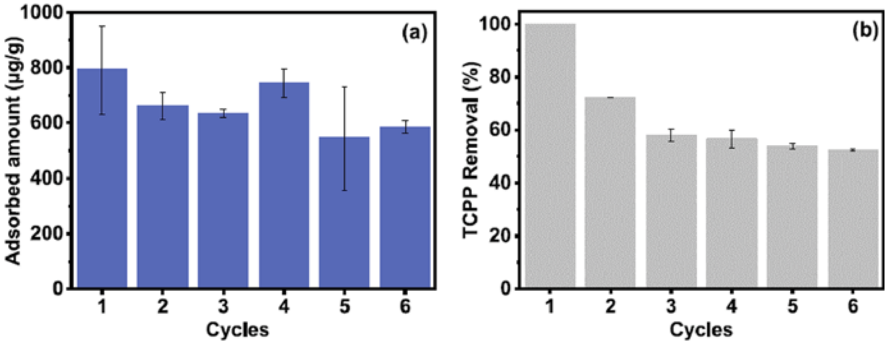


Fig. 7 Removal of trichloropropyl phosphate by the C/nano-Fe_3O_4 composite in six successive (**a**) adsorption cycles and (**b**) degradation cycles in the Fenton-like system (Wang et al. 2021b)

halogenated branched chains on triphosphate. This attack resulted in the mono- and di-ester phosphates. It was proved that the C/nano-Fe_3O_4 composite can be efficiently reused in successive adsorption cycles, as shown in Fig. 7.

Iron has an integral role in the chemical degradation of environmental pollutants. According to Karn et al. (2009), this is due to its reducing properties as an electron donor, so it possible to employ it for the remediation of any contaminant that can be degraded by reduction. During the reaction, iron nanoparticles are oxidized to ferric/ ferrous ion and the halogenated organic contaminant is reduced. Zhang (2003) reported that nanoscale Fe particles are very effective for the transformation and detoxification of a variety of common environmental pollutants, including chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls. The mechanism summarized as: Fe-chemical reactions that lead to an increase in pH and a decrease in the solution redox potential created by the rapid consumption of oxygen, other potential oxidants, and the production of hydrogen. Successful degradation of pesticides such as 2,4-dichlorophenoxyacetic acid using Fe_3O_4 nanoparticles have also been reported by Fang et al. (2011). Fe_3O_4 nanoparticles not only degraded 2,4D in soils but also increased the soil microbial populations and enzyme activities. Iron nanoparticles can be used to remediate surface contaminants like petrochemical compounds and even sub-surface contaminants like pesticides, organic solvents, fertilizers, and heavy metals.

1.3 Electrocatalytic Degradation

During electrochemical oxidation technology, the most active hydroxyl ($^{\cdot}OH$) radicals can be formed with a predominant rate at ambient conditions. Therefore, electrooxidation can be considered as one of the most common and powerful method for treatment of organic pollutants (Chai et al. 2014). Depending on the type of the anode material, the rate of $^{\cdot}OH$ radical formation can be assigned and detected.

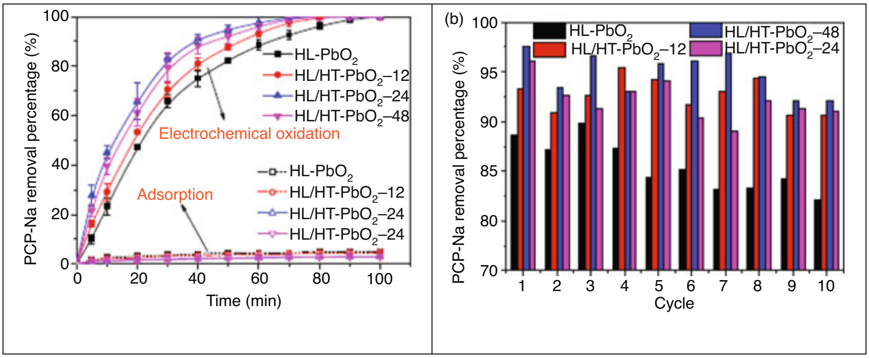


Fig. 8 Variation of removal efficiency of sodium pentachlorophenate with time (**a**) and the recyclability (**b**) (Duan et al. 2020a)

There are two common types of materials that can be employed as anodes in electrochemical oxidation, as reported in the literature, either active materials (Pt, IrO_2, and RuO_2) or inactive anodes (SnO_2, β-PbO_2, and B-doped diamond). Unexpectedly, inactive materials have a higher electrochemical activity as anodes than the active ones, this is because of their higher oxygen evolution potential, which minimize the occurrence of the undesirable side reaction and oxygen evolution reaction. Thus, an increased rate of ˙OH radical production can be observed during the electrochemical oxidation process. An additional factor that can greatly affect the rate of the generation of ˙OH radicals is the specific surface area. The electrocatalytic activity of the anode can be greatly improved by increasing its specific surface area. Fe–Ce co-PbO_2 nanocomposite on Ti/TiO_2 nanotube electrode was fabricated via the pulse electrodeposition by Xu et al. (2018). It was found that the prepared electrode has a powerful electrochemical activity due to its high specific surface area and small grain size. Nano-sized Ce–PbO_2 was also obtained on NiO-modified Ti/TiO_2 nanotubes electrode via the electrodeposition method (Wang et al. 2017). This anode exhibited also a high surface area and, in turn, enhanced electrochemical oxidation performance. These studies confirmed that the small grain size of PbO_2 largely enhanced the electrochemical activity of the prepared electrodes as it offered active sites for the electrochemical oxidation reactions. An additional activity can be resulted by using nano-sized PbO_2, for example, nano-PbO_2 powder, prepared via the hydrolysis of lead acetate, has a large specific surface area and, thus, high electrochemical activity in lead-acid cells (Morales et al. 2004). PbO_2, of a high degree of crystallinity, can be prepared after being treated to a hydrothermal process for a long period. The obtained material allowed a high rate of ˙OH radical generation due to its high oxygen evolution potential, and in turn, a higher electrochemical activity, than the conventional PbO_2 anode, prepared by the electrodeposition (Duan et al. 2020a). The prepared PbO_2 anode showed a higher sodium pentachlorophenate degradation rate, and the efficiency was 2.7 times than that at electrodeposited PbO_2 anode (Fig. 8).

Table 2 Removal % values, calculated from absorbance as well as COD data, at different operational conditions for the electrocatalytic degradation of Congo red dye at polyaniline/TiO_2 nanocomposite (Emran et al. 2018)

pH value	4	6	7	8	10
%Removal, absorbance	99.39	99.70	97.23	99.70	23.14
%Removal, COD	96.87	97.63	96.66	97.14	25.25
Electrolysis time, min	5	10	20	30	60
%Removal, absorbance	19.33	24.73	73.48	97.23	99.62
%Removal, COD	17.37	25.23	75.53	96.66	98.25
Applied current density, A m^{-2}	0.5882	1.7647	2.9412	4.1176	5.8824
%Removal, absorbance	73.85	97.23	98.65	99.51	99.49
%Removal, COD	72.53	96.66	97.29	97.25	97.41
Initial dye conc., mg L^{-1}	100	200	250	300	350
%Removal, absorbance	99.11	97.23	92.91	88.31	82.32
%Removal, COD	98.29	96.66	92.76	87.92	80.94

Polyaniline/TiO_2 nanocomposite has been employed as an efficient anode for Congo red degradation by the electrochemical oxidation. The degradation efficiency can be affected by dye solution pH and concentration, electrolysis current, and time (Emran et al. 2018). Table 2 summarizes the optimum conditions of the previously mentioned factors, that when being applied, the highest degradation efficiency can be resulted, Table 2. It was found that high removal % resulted at pH 7, electrolysis time 30 min, and current density 1.7647 A m^{-2}.

B-doped diamond, Ti/$Ru_{0.3}Ti_{0.7}O_2$, and Ti/Pt anodes were used for verifying the efficiency of the electrochemical oxidation process for the removal of the industrial textile disperse yellow 3 dye in sulfate and chlorine medium (Salazar et al. 2018). Results are obtained at values of pH about 2.3, 7.0, and 10.0 and different current densities (40 and 60 mA cm^{-2}) at 40 °C using Na_2SO_4 as electrolyte, and the anodic oxidation process was faster at the beginning of all electrocatalytic materials. In Na_2SO_4 aqueous solutions, B-doped diamond is more efficient and reaches more than 90% of total organic carbon (TOC). The color decay was independently of the current density and pH and supporting electrolyte. For other anodic materials, color decay was up to 50% and TOC was eliminated. In NaCl medium, the presence of chlorine reactive species increases the degradation of organics, because a complete mineralization is reached in NaCl medium with Ti/$Ru_{0.3}Ti_{0.7}O_2$ and B-doped diamond at short electrolysis time, significantly reducing process costs. The efficiency of Cl-mediated electrochemical oxidation was confirmed by the determination of concentration of main active chlorine species produced at all electrode materials, determining that it depends on the nature of electrode material and pH conditions. In addition, at Ti/$Ru_{0.3}Ti_{0.7}O_2$ and B-doped diamond anodes, more efficient homogeneous catalytic reactions are favored for removing organic matter in solution. A cost comparison for each electrocatalytic material under different experimental conditions was realized exhibiting the lowest energy consumption and electrolysis time in NaCl medium. Based on the results obtained, the electrochemical elimination of dye and the profile of the carboxylic by-products formed depend on the nature of material, pH, and supporting electrolyte (Salazar et al. 2018).

The solution of acid red 27 was treated by V/TiO_2 (vanadium doping from 0.05 to 0.30 V) anode electrode in electrocatalytic system (Chang et al. 2020). Results demonstrate that acid red 27 can be effectively degraded by the nano-V/TiO_2 electrodes; the highest removal efficiency of color and TOC reached 99% and 76%, respectively, under 0.10 V. The nano-V/TiO_2 electrode with high specific surface area facilitated the electrocatalytic degradation. The current density of 25 mA cm^{-2} was found to be the optimum operation for this electrocatalytic system, whereas the oxygen was increased with the current density. The electricity consumption of pure TiO_2 and nano-V/TiO_2 electrode in this electrocatalytic system was around 0.11 kWh L^{-1} and 0.02 kWh L^{-1}, respectively. This implies that the nano-V/TiO_2 electrode possesses both high degradation and energy saving features. Moreover, the nano-V/TiO_2 electrode shows its possible repeated utilization.

A carbon felt with a highly porous structure and a conventional planar graphite sheet were used as electrode substrate for PbO_2 anodes (Rahmani et al. 2021). The electrocatalytic degradation of diuron ($C_9H_{10}C_{12}N_2O$) using three-dimensional porous carbon felt/PbO_2 anode was modeled and optimized by a rotatable central composite design. Parameters affecting diuron removal were optimized by an rotatable central composite design method. The interaction effect of the initial pH of the solution and the concentration of Na_2SO_4 electrolyte is shown that, at a concentration of 0.04 M Na_2SO_4, the reaction time of 30 min and the current density of 10 mA cm^{-2}, by increasing the initial pH of the solution from 3 to about 5.7, the diuron removal efficiency increased from about 79.9 to 83.2%. After optimizing the process, the ability of porous carbon felt/PbO_2 and planar graphite/PbO_2 anodes to degrade and mineralize diuron was compared. The results under optimal conditions proved that the kinetics of diuron removal using carbon felt/PbO_2 anode was three times faster than the graphite/PbO_2 anode. The energy consumed for the complete mineralization of diuron was 2077 kWh kg^{-1} TOC for carbon felt/PbO_2 and 65% of the TOC for graphite/PbO_2. They effectively improve the kinetics of the electrochemical degradation process of the carbon felt/PbO_2 explained according to more stability (115 h vs. 91 h), larger surface area (1.6287 m^2 g^{-1} vs. 0.8565 m^2 g^{-1}), and higher oxygen evolution potential (1.89 V vs. 1.84 V) compared to the graphite/PbO_2. The electrochemical degradation of diuron with carbon felt/PbO_2 anode was monitored every 15 min by the cyclic voltammetry technique. Several different paths were proposed for the degradation of diuron. Possible diuron degradation pathways are suggested in Fig. 9. As can be seen, ·HO radicals as the main oxidizing species lead to the degradation of diuron. This degradation mechanism is performed in five different ways. The aromatic ring and carbonyl, dimethyl urea, and amide groups are the main targets of HO· radicals for diuron degradation. In the proposed pathways for diuron degradation, the aromatic ring and groups of carbonyl, dimethyl urea, and amide were the main targets for HO radical attacks.

In addition, anodic oxidation can be used as a hybrid process with other one for efficient removal of pollutants and obtaining better decontamination (Hua et al. 2021). The typical hybrid processes can be classified into two main kinds, the first

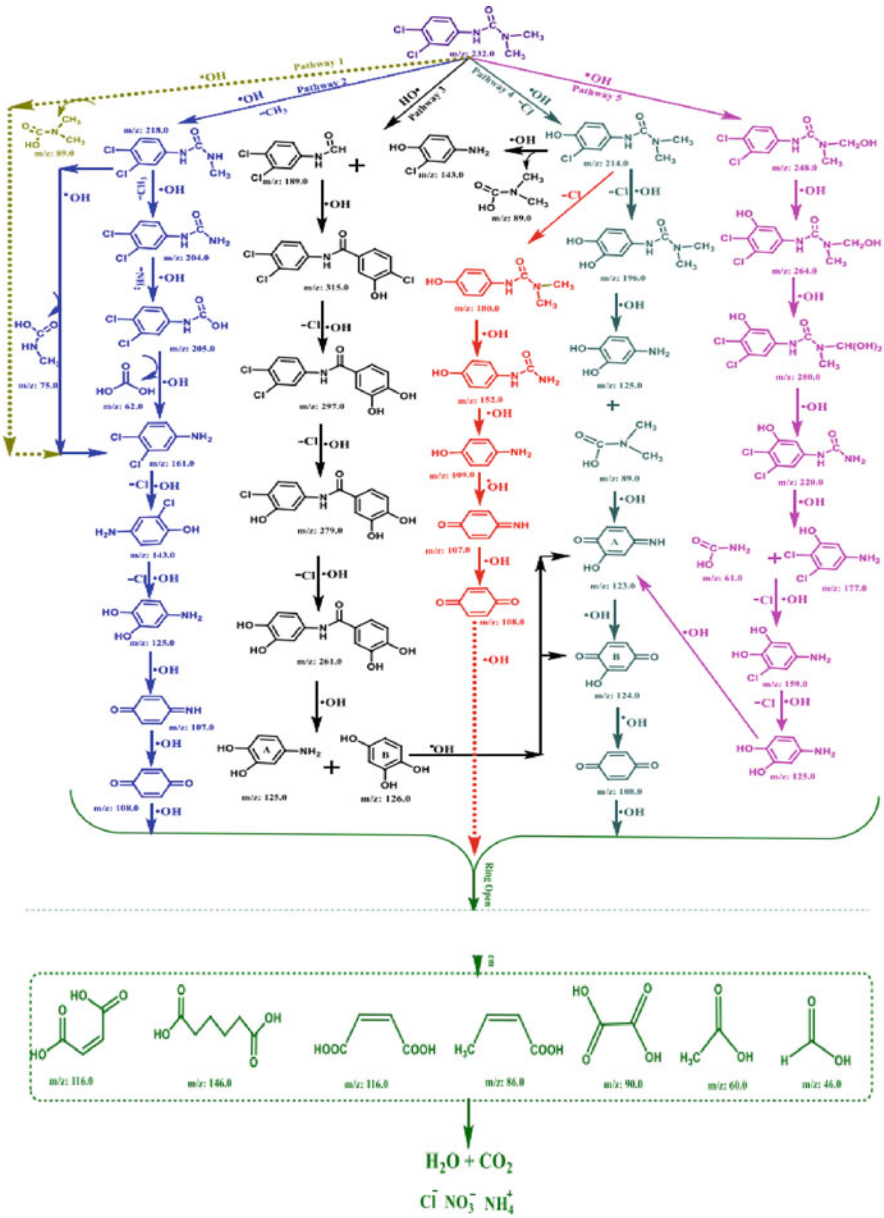


Fig. 9 Proposed pathways for diuron degradation (Rahmani et al. 2021)

is the coupling of the anodic oxidation with another process in the same cell, such as coupling with the electro-Fenton (EF), or photoelectron–Fenton (PEF) or the ultrasound oxidation (US). The second is a combined process including the anodic oxidation with another physical (adsorption or ultrafiltration), chemical (ozonation

Table 3 Typical hybrid processes (Hua et al. 2021)

Type	Hybrid process	Main results	Ref.
Coupling	AO/EF	AO:40%TOC AO/EF:55.1% TOC EF–AO–DSA:64.3%TOC PEF:53% of methyl orange	Duan et al. (2020b)
	AO/PEF	PEF:53% of methyl orange AO/PEF:71% of methyl orange	Olvera-Vargas et al. (2021)
	AO/US	AO:60.6% of oxacin AO/US:95% of oxacin	Becerril-Estrada et al. (2020), Patidar and Srivastava (2020), Chennah et al. (2020)
Combined process—AO as pretreatment	AO + Wetland	AO:25% TOC AO + Wetland:61% TOC	Saha et al. (2020)
	AO + MBR	AO:55%of ibuprofen AO-MBR:99% of ibuprofen	Ouarda et al. (2018)
Combined process—AO as pretreatment	AO + Adsorption	Adsorption:20% mecoprop AO+ Adsorption: –100% mecoprop	Pedersen et al. (2019)
	AO + UF	AO:13% DCO AO + UF:53% DOC	Gonzalez-Olmos et al. (2018)
	AO + Ozonation	AO:92.1% TOC at 120 min AO + Ozonation: 98.5% TOC after 60 min	Amado-Piña et al. (2017)
	AO + UV	AO:84.71%TOC AO + UV:96.25% TOC	Montanaro et al. (2017)
Combined process—AO as advanced treatment	ECO + AO	ECO + AO:84.6% TOC ECO:56%COD ECO + AO:72% COD	Gengec (2017), Dobrosz-Gómez and Gómez-Garcíab (2020)

or UV irradiation), or biological process, such as membrane bioreactor (MBR). Table 3 summarizes examples of these hybrid processes with important data and results.

1.4 Adsorption

Adsorption can be used effectively for water decontamination from organic pollutants. In addition to the simplicity and cost effectiveness advantages offered by adsorption, the technique is also nonselective and insensitive to harmful materials, and the adsorbents can be easily recovered and possibly reused several times. Nanomaterials and nanocomposites can be used as efficient sorbents, without the concerns of the toxicity of these materials. The adsorption modes of para-nitrophenol, onto the anatase TiO_2 (100) surface, were investigated (Wahab 2012). The density states at both valence and conduction bands of TiO_2 influenced the adsorption mechanism of para-nitrophenol at the Ti(IV) and Ti(V) sites because of the organic–cluster interactions. It was found that a para-nitrophenol molecule can interact with the surface of TiO_2 through the oxygen atoms of an NO_2 and/or an OH group, and no π-interaction with the aromatic ring can exist. The distribution of charges around the para-nitrophenol molecule is related to the geometry of the organic–cluster, which is affected by the adsorption process. Nanotitanium oxide–bentonite–chitosan composite can be used to obtain enhanced the removal of antibiotics, such as levofloxacin (LEVO) and ceftriaxone (CFT) (Mahmoud et al. 2020). The extraction % can be affected by pH, time, initial concentration of the studied antibiotic, and the presence of interferences. All these factors are studied and optimized, and the maximum % values were 90.2% and 93.5% at pH values of 4 and 5, for LEVO and CFT, respectively, within 10 min. Langmuir, Freundlich, and Temkin adsorption models were used to explain the extraction mechanism. Langmuir model can perfectly fit the adsorption data as indicated by the correlation coefficient values, 0.952 and 0.987 for LEVO and CFT, respectively. Adsorption is spontaneous and endothermic, as concluded from the calculated thermodynamics parameters. The adsorption followed the *pseudo*-second-order, as indicated by the correlation coefficients values, 0.999 and 0.997 for LEVO and CFT, respectively. Results showed that the prepared nanocomposite was effectively extracted LEVO and CFT from wastewater with % values of 83.2% and 79.0%, respectively. The suitable performance of the nanocomposite for removal of LEVO and CFT from various samples was proved, as shown in Table 4.

A nanocomposite composed of MgO/palm shell-activated carbon was prepared by dropwise mechanism. Then, the nanobiosorbent was employed as an efficient adsorbent for the removal of anthracene from water (Jagadeesan et al. 2019). It was found that an adsorbent dose of 6 g/L at 30 °C and initial anthracene concentration of 25 mg/L constituted the optimum conditions for the highest removal performance.

Table 4 Application of nanotitanium oxide–bentonite–chitosan composite for removal LEVO and CFT from water (Mahmoud et al. 2020)

Antibiotic	Concentration	pH	% Extraction after third run		
			Tap water	Sea water	Wastewater
Levofloxacin	5.0 mg L^{-1}	4	95.00	54.50	83.20
Ceftriaxone		5	92.80	40.00	79.00

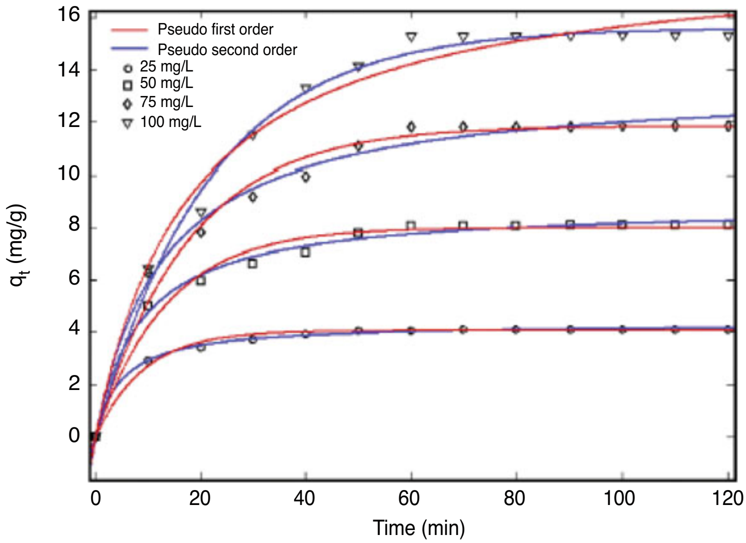


Fig. 10 Fitting of the adsorption kinetic data of anthracene by nano-MgO carbon nanocomposite (Jagadeesan et al. 2019)

The adsorption mechanism can be explained based on Freundlich isotherm model. The equilibrium was achieved in 1 h and the adsorption data fitted well the pseudo-second-order model, as shown in Fig. 10. It was possible to regenerate the nanobiosorbent successively. A deviation of about 3.02% from predicted experimental removal % values with a confidence level of 95% is reported.

Nano-ZnO/graphene oxide/nanocellulose composite can be used as an effective adsorbent and also in the photodegradation of ciprofloxacin (Anirudhan and Deepa 2017). A batch experiment was used to collect the adsorption data. The operation conditions were optimized to get the highest removal % (pH = 5.5 and adsorbent dose of 2.0 g/L), as shown in Fig. 11. The adsorption followed second-order kinetics, and the equilibrium can be achieved within 2 h. The mechanism of interaction between the nanocomposite and the studied drug can be explained according to Sips isotherm model. On the other hand, the degradation followed first-order kinetics. A maximum degradation efficiency of 98.0% was obtained at an optimum pH value of 6. Zinc oxide-incorporated graphene oxide/nanocellulose can be successively used after five consecutive cycles.

Nanocomposites of polyaniline with different supporting nano-oxides, SiO_2, TiO_2, Al_2O_3, and Fe_3O_4 are prepared by the chemical polymerization method (Ali et al. 2017). Prepared nanocomposites are tested as sorbents for the removal of Congo red from water, and exhibit a good adsorption performance at neutral conditions. Langmuir isotherm model can fit well the adsorption data of the dye onto different nanocomposites. The dye uptake is largely affected by the amount of polyaniline loaded on the supporting nano-oxide. It was found that by using Al_2O_3, the largest amount of the polymer exists in the composite, resulting in the most

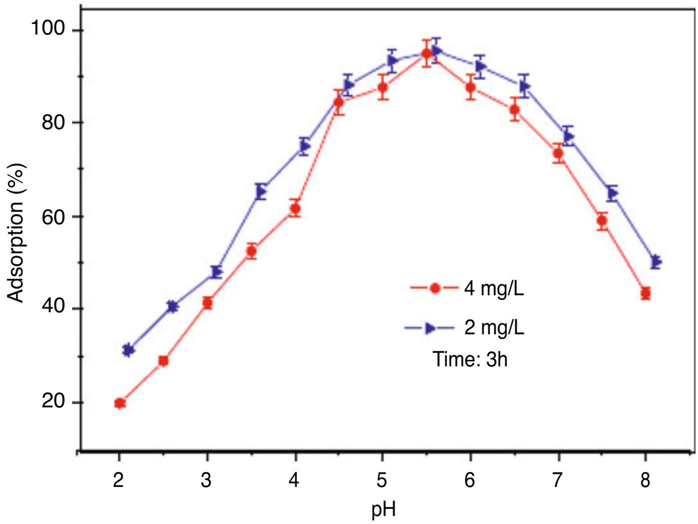


Fig. 11 pH optimization in adsorption % of ciprofloxacin onto zinc oxide incorporated graphene oxide/nanocellulose (Anirudhan and Deepa 2017)

Table 5 Calculated entropy change (ΔS), enthalpy change (ΔH), and activation energy (E_a) for adsorption of Congo red onto various nanocomposites (Ali et al. 2017)

Composite	ΔH, kJ mol^{-1}	ΔS, kJ mol^{-1}K^{-1}	E_a, kJ mol^{-1}
Polyaniline/SiO_2	70.63	0.249	73.18
Polyaniline/TiO_2	51.73	0.190	54.28
Polyaniline/Al_2O_3	30.08	0.124	32.63
Polyaniline/Fe_3O_4	31.40	0.128	33.95

efficient sorbent. The adsorption followed intra-particle diffusion and the second-order kinetics models. The adsorption process is an endothermic and has a chemisorption mode as indicated by the positive sign of enthalpy change (ΔH) and calculated activation energy (E_a) values, as shown in Table 5. The positive sign of entropy change (ΔS) indicates the increased random at nanocomposites interface during Congo red adsorption.

Salipira et al. (2007) have reported the use of a novel cyclodextrin-based nanoporous polymers containing functionalized carbon nanotubes. These multiwalled carbon nanotubes, functionalized with a mixture of nitric and sulfuric acid, successfully removed the trichloroethylene, dioxins, and polychlorinated biphenyls from water at parts per billion levels. GC–MS results have demonstrated the ability of nanoporous polymers in the absorption of trichloroethylene from water at very low concentration. The surface properties of these polymers are probably an important factor in determining the extent to which the polymer could absorb the organic pollutants from water.

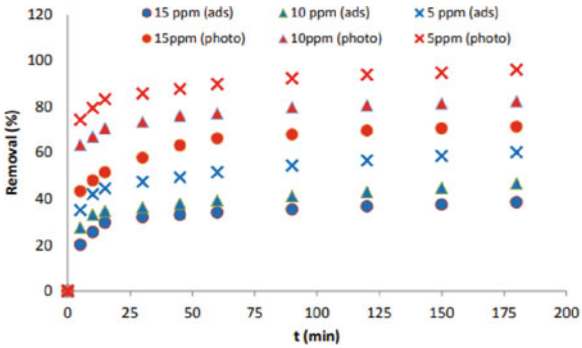


Fig. 12 Effect of initial dye concentration on the adsorption and photodegradation of methylene blue on 5-sulfosalicylic acid–TiO_2 (pH = 6, T = 298 K and contact time 180 min) (Mohammadi and Karimi 2017) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

TiO_2 nanoparticles were successfully modified by 5-sulfosalicylic acid through chemisorption process and used for the removal of methylene blue from aqueous solution by photocatalytic activity and adsorption properties (Mohammadi and Karimi 2017). As shown in Fig. 12, the influence of initial dye concentration on the adsorption and photodegradation efficiency of methylene blue, the removal efficiency of the dye molecules by 5-sulfosalicylic acid–TiO_2 nanoparticles, decreased with an increase in the dye concentration.

This is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration. Therefore, the remaining amounts of dye molecules will be higher for high initial concentrations of dye. In contrast, the photodecolorization of methylene blue decreases with increasing of the initial dye concentration. The presumed reason is that, when the initial dye concentration is increased, more and more dye molecules are adsorbed on the surface of 5-sulfosalicylic acid–TiO_2 nanoparticle. Therefore, the generation of OH free radicals will be reduced, since the active sites for adsorption were covered by dye molecules. The calculated thermodynamic parameters by the effect of the temperature on the dye removal efficiency showed that adsorption and photodegradation processes of the dye using the 5-sulfosalicylic acid–TiO_2 nanoparticle are spontaneous. The kinetic study indicated that the photocatalytic degradation and adsorption of the dye using the 5-sulfosalicylic acid–TiO_2 nanoparticles can be described by pseudo-first-order and pseudo-second-order kinetic models, respectively, and the adsorption of methylene blue onto the 5-sulfosalicylic acid–TiO_2 adsorbent is better described by the Temkin isotherm model than the Langmuir and Freundlich isotherms (Mohammadi and Karimi 2017).

In similar study, the adsorption capacity and photocatalytic activity of activated carbon supported titania composites were explored through the removal of phenol, naphthol blue black, and reactive black 5 (Nguyen et al. 2020). The Langmuir adsorption isotherms (Fig. 13) of model pollutants (phenol, naphthol blue black,

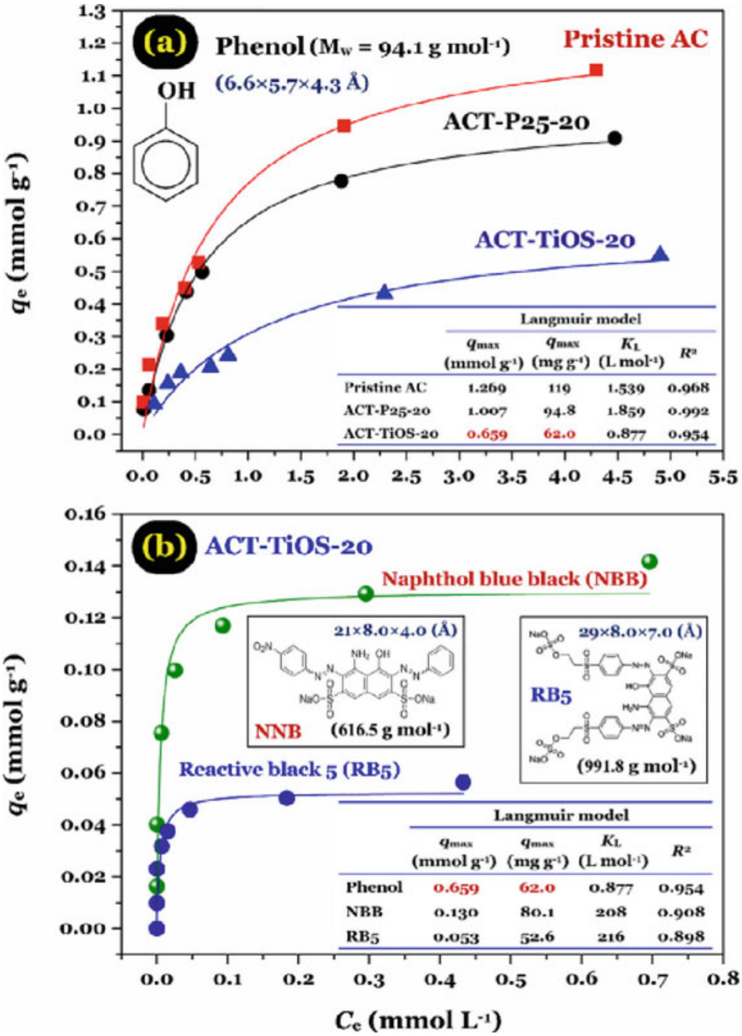


Fig. 13 Adsorption isotherms of (**a**) phenol on activated carbon, activated carbon titania–TiOS-20, and activated carbon titania-P25–20 composites as well as of (**b**) naphthol blue black, and reactive black 5 on ACT-TiOS-20 composite (Nguyen et al. 2020) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

and reactive black 5 were used to describe the adsorption behavior of various adsorbates. The adsorption abilities of the materials were consistent with their order of surface area: activated carbon (1316 $m^2\ g^{-1}$) > activated carbon supported titania P25–20 (1101 $m^2\ g^{-1}$) > activated carbon supported TiOS-20 (496 $m^2\ g^{-1}$). This result suggests that pore filling played a crucial role in the adsorption mechanism of phenol on prepared samples.

The conditions for the occurrence of the synergism of adsorption and photocatalysis in the removal of the three organics by activated carbon titania composites were based on their individual kinetics of adsorption and photocatalysis. The amounts of phenol (the smaller organic) adsorbed on the activated carbon titania composites decreased dramatically with the increasing weight percentage of Ti. This could be because the more the Ti was loaded on activated carbon, the more adsorption sites were covered, which led to a decrease in the surface area and pore volume of the activated carbon titania composites. On the other hand, the larger organics (naphthol blue black, and reactive black 5) were more difficult to enter into the pores and thus were primarily adsorbed on the external surface of the adsorbent. Kinetic analysis revealed that the behavior of adsorption-assisted photocatalysis was significant only when the initial rates of adsorption and degradation were comparable. This strongly depended on the properties of the adsorbents (e.g., surface area and pore size) and the organics (e.g., molecular size and chemical structure). The reusability tests of activated carbon titania composites indicated their promising application potential for the removal of organics from aqueous solutions due to their high chemical and operating stability.

2 Conclusion

Nanometal oxides can be used efficiently for the removal of organic pollutants, such as dyes, pesticides, and other organics, from wastewater in several ways. Many of nanomaterials can act as photocatalysts as it have a proper bandgap for electron–hole pairs formation upon being irradiated to sunlight. Furthermore, it is non-toxic and offers a good stability in water. Oxygen radicals formed by the reduction of oxygen in the conduction band by the photo-generated electrons, and the hydroxyl radicals formed by the reaction of holes with adsorbed water in the valence band can strongly degrade the organic pollutants into non-harmful carbon dioxide and water. Recent literature introduced in this chapter focus on how to control these radicals formation by forming nanocomposite-based metal oxides. Nano-oxides can also act as chemical oxidants and efficient anodes for the catalytic and electrocatalytic degradation of organic pollutants, respectively. Nano-oxides have high crystallinity, high oxygen evolution potential, and a lot of active sites, resulting in strong OH radical generation capacity and high electrochemical activity. In addition, nano-oxides can act as powerful adsorbents for the removal of organic pollutants. Adsorption process is characterized by simplicity, non-selectivity and insensitivity to harmful materials, as well as the easily recovery of sorbents materials. Several factors can affect the adsorption process, such as pH, contact time, temperature, and the presence of interferences. These factors should be studied and optimized to attain the highest possible adsorption performance of the nanomaterials. It is worth to mention that the use of nanometal oxides as sorbents provided a unique and significant research discipline.

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Accumulation of Engineered Nanomaterials in Soil, Water, and Air

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1 Introduction

In the early 2000s, the beginning of "Nano-era" has led to the initiation of various research programs in nanotechnology field which increased the engineered nanomaterials (ENMs) production steadily (Roco 2003). ENMs possessed unique characteristics such as high reactivity and surface area-to-volume ratio when compared with bulk materials, where it allows utilization of various technologies. The production and incorporation of ENMs have been elevated subsequently with increase of consumers that lead to the release of ENMs to the environment. The commercially available ENMs are zinc oxide (ZnO), titanium dioxide (nano-TiO_2), carbon nanotubes (CNTs), silver (nano-Ag), gold (nano-Au), graphite, C60 fullerenes, and silica (nano-SiO_2) and the products included are inkjet printer ink, plastics, cosmetics, sunscreens, sporting goods cleaning materials, and textiles (Shah et al. 2010).

ENMs are considered to be one of the newly formed non-biodegradable pollutants. The usage of ENMs intensively has led to the raise of concerns related to the possible build up in ecosystems and food supply. In addition, the concerns related to agriculture are greater, where the soils are exposed to products that contain ENMs intentionally. The nanomaterials form and state determines its fate, which influences it properties, such as particle density, aggregation behavior, and solubility. Due to

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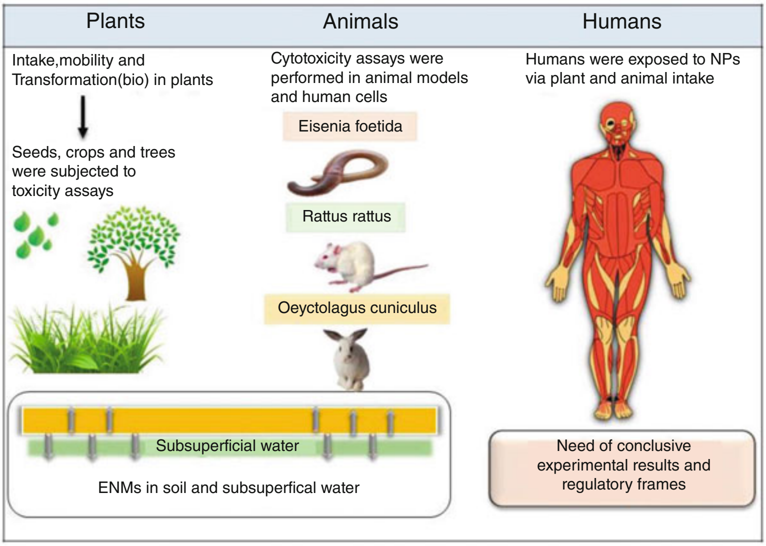

Fig. 1 Exposure of ENMs during the lifecycle

the special characteristics, the ENM usage has increased rapidly in industrial and agricultural products, as well as in environmental systems. Also, the rapid usage and expansion lead to the release of ENMs in environment particularly in the aquatic ecosystems, where it is ultimate sink. ENMs present in the environment may interact with human through direct or indirect way. Thus, there is a vital need to understand the fate, transformation, mobility, and behavior of ENMs in air, water, and soil. Figure 1 shows the exposure to ENMs during their lifecycle.

1.1 Fate of ENMs in Soil

Soil acts as major sink for ENMs. Several factors determine the transportation and fate of ENMs entering into the soil, such as the composition, pH, morphology, and the cation exchange capacity, size, chemical composition, zeta potential, and surface coating of ENMs. It is essential to understand the ENM dynamics in soil. Figure 2 shows that the factors influencing the fate, transportation, and retention of ENMs in soil.

1.2 Soil Type

In last few decades, irreversible changes occurred in the soil due to its contact with chemical contaminants originated because of anthropogenic actions. These irreversible changes are long termed, stable, and the physical and chemical properties of soil

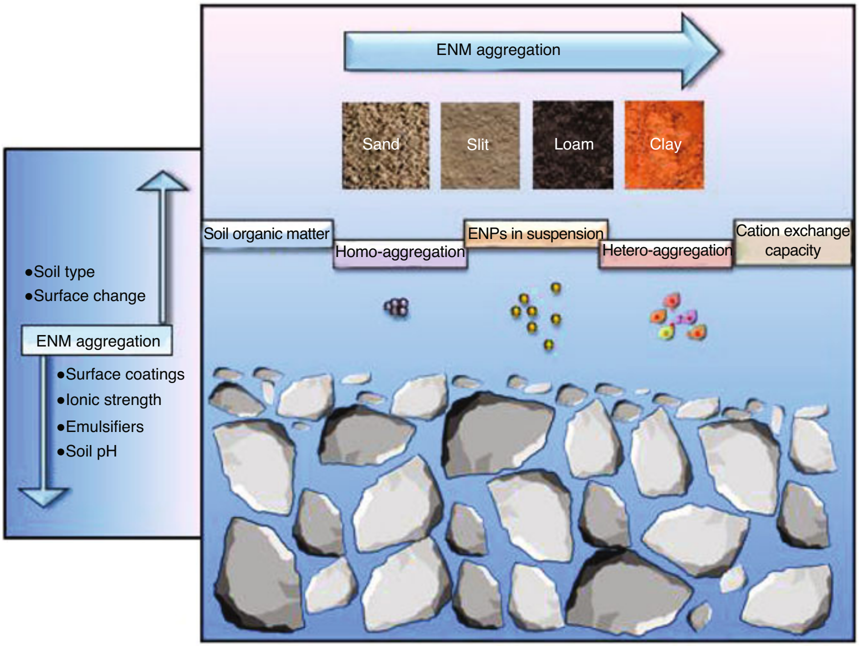

Fig. 2 Factors influencing the fate, transportation, and retention of ENMs in soil

transforms persistently, where it is resistant to remediation procedures and natural attenuation.

The characteristics of the soil are important for determining the fate of ENMs such as the slit, clay, porosity, loam, organic matter, and grain size. ENM's retention and transport have been influenced greatly by soil. ENMs get coated with organic matter such as humic acids or fulvic acids present in the soil environment, and it leads to the increase in particle size. Due to soil-derived coating, the particle undergoes a change in its zeta potential from positive charge to negative charge. Some of the clay particles or natural organic matter in the native form dissolves in ionic state resulting in heteroaggregation. Hence, the available surface area for the chemical interaction is reduced.

It is estimated by Keller et al. (2014) that the total ENM's waste ending up in landfill is 63–91%, in which 8–28% are deposited in soil. It is clear that the exposure of ENM to soil is more vulnerable (Keller et al. 2014). From the previous studies, it is well-understood that the behavior of ENMs differs based on the physical and chemical properties (Keller et al. 2014). The ENM transforms into different forms in plants and soil. Servin et al. (2013) reported the interaction of ENM with components of soil and other co-contaminants. The multiple factors associated may be the reason for the contradictory findings in the literature such as the species used, region, and the measurement of endpoints. The ENM toxicity or direct uptake is not only the factor impacting the growth of plant. In general, plants form complex symbiotic relationship with microbes present in the Rhizophore (nitrogen fixing bacteria). The plant gets affected indirectly due to the ENM impact on these species (Gardea-Torresdey et al. 2014). The microbial population disturbances could lead to nitrogen starvation resulting in stunted growth.

1.3 Accumulation of NPs in Soil and Plant Tissues

Agriculture makes more profit by developing very effective and less contaminant agrochemicals by nanoformulation. Also, the nanosensors help in detecting biotic or abiotic stress before it affects the output (Giraldo et al. 2019). Nanotechnology has facilitated the development of intelligent nanotools and high tech agriculture fields (Kumar and Arora 2020; Giraldo et al. 2019). The development of these technologies can transform the changes in the agriculture fields, which can create a significant impact on the modern agriculture (Arora 2018; Kwak et al. 2017). Currently, the research in the agriculture fields focuses on developing nanoagrochemicals including nanofertilizer and nanopesticide (Kah 2015). These materials offer the release of agrochemicals in a controlled manner and the selective delivery of macromolecules. The fertilizers and pesticides can integrate efficiently with the carriers which are in nanoscale and the applied compounds can lead to reduction in its amount without the impairment in application (Parisi et al. 2015). The nanoagrochemical application seems to be important for the promotion of modern agriculture. In the food chain, plants are the important factor as it is the producer in the primary trophic level in the ecosystem. The bioaccumulation and the NP impact on long term to the plants can affect the food chain with unknown consequences to humans (Rajput et al. 2018b). The studies were reported that NP's uptake can lead to its accumulation in edible tissue of crop plants (Da Costa and Sharma 2016). The accumulation of original metal ions or NPs can cause changes in the physiochemical properties of the plant (Cota-Ruiz et al. 2018; Patel et al. 2018). The NP accumulation can alter the physiological process of plants, and it can affect the cell integrity, nucleic acids, lipids, and sub-cellular organelle organizations and modify the proteins content (Rajput et al. 2018a, 2018b, c). The wide range of applications of NPs can increase the issues concerned with the health, ecology, and safety point of view (Garner et al. 2017). Till now, the negative impact of these NPs on human health is uncorroborated and speculative (Baranowska-Wojcik et al. 2020). The massive disposal of NPs in several hundred tons every year that made the experts and researchers worried. These released NPs can be detected according to the normative documents recommended recently in soil, air, objects, fungi, algae, and water objects (Gupta and Xie 2018; Keller et al. 2017). The NPs reached into the soil system undergo a transformation in its biogeochemical cycles (Chen et al. 2018; Servin et al. 2017).

1.3.1 Soil as Sink for NPs

The pathway followed by the NP's entry in the soil can be characterized through its entry, content of accumulation and migration. The entry of NPs in the soil via the precipitation in the atmosphere, sedimentation in dust and aerosol form, leaves abscission and direct absorption of gases (Gladkova and Terekhova 2013). In general, NPs released from the anthropogenic sources can be categorized into point and non-point sources. The NPs disperse freely into the environment by outleting it directly to the environment or NP degradation. The remediation of contaminants using NMs causes the discharge of NPs significantly into the environment (Attia and Elsheery 2020). The landfills and waste water discharge plants are also responsible for the release of NPs in the form of discharged effluents or concentrated sludge. The other ways of exposure in the environment are leakages or spill out during the transport and production steps of NPs (Gottschalk et al. 2013).

Nanopesticides, nanofertilizers, hydroponic solutions, and seed treatment are the wide applications which concern the soil and agro-environment expecting to open a new way for the NP's release into the cultivated soils. According to this, the speculation says that 95% of the copper used are ended up eventually into the aquatic sediments and soils with the concentrations of 500 μg/kg (Keller et al. 2017). In case of ZnO, the concentration estimated was 16 μg/kg (Feng et al. 2016), whereas the concentration of CeO_2 NPs varied from 0.01 to 4.3 mg/kg (Boxall et al. 2007). The information provided above only tells us about the necessary to study the route which can alter the NP property and facilitate the release into the nature. During its release into the agro-environment, NPs undergo immediate transformations facilitating its accumulation in the soil. The transformation speed differs depending on the state of its aggregation. The soil constituents and its properties such as water content, pH, or organic matter can mediate the dissolution process of the NPs (Benoit et al. 2013). The bioavailability of NPs is depended mainly on its transformations into the soil. The NPs in its dissolved form show higher risk and bioavailability in the environment. The environmental risk can be associated and depends on the chemical species and bioavailability of NPs in the soil (Lead et al. 2018). Hence, it is a critical issue to evaluate the bioavailability of NPs rapidly and accurately in the soil.

1.3.2 Influence of ENMs in Germination, Growth, and Yield of Plant

The accumulation of NPs in the edible plant tissue can affect the health of the human through the food chain considered to be one of the important critical issues. The interaction of NPs with the plant roots can cause translocation in the aerial parts and also cause accumulation in subcellular or cellular organelles. The first step of bioaccumulation is the adsorption of NPs by plant roots (Nair and Chung 2015). During this competition between the ions, the adsorbed CuO NPs cannot be desorbed (Rajput et al. 2018a). The evaluation of different NPs by researchers suggests that the accumulation of NPs in plants occurs by adsorption through roots and is distributed through the plant tissue with some modifications, including the crystal phase dissolution, bioaccumulation, and biotransformation (Peng et al. 2015). The studies were also reported that NPs can be taken up and tend to accumulate in the plant cells (Peng et al. 2015; Da Costa and Sharma 2016). These discussions suggest that the NPs entered via root and shoot tissues.

The presence of ZnO NPs in the shoots and roots has also been confirmed in *M. sativa* (Bandyopadhyay et al. 2015) and *B. juncea* (Rao and Shekhawat 2016). The accumulation of NPs in plant tissue can adversely affect the physiological process in plants and also alter the cellular and subcellular organizations (Fedorenko et al. 2020). It modifies the lipids, nucleic acids, and proteins contents by generation of reactive oxygen species (Halliwell and Gutteridge 1985).

The accumulation rate of NPs in the plants root can influence the NPs property and also the environmental conditions (Chen 2018). Ag uptake through biosolids-amended soil has increased the Ag NPs concentration in *L. sativa* plant roots and shoots (Doolette et al. 2015). In *Z. mays*, the accumulation of CeO_2 NPs is found to be low in roots (Zhao et al. 2012a, b). The NP's bioavailability in the rhizophore has increased because of the microbial siderophores occurrence and root exudates. Also, it has been known that microorganisms and plants produce ligands for solubilizing minerals from the inadequately available sources. Microbial siderophores are formed from various organisms, where it is low molecular weight organic compounds for chelation of iron under restraining conditions of iron. Recently, the studies have shown that the siderophores provides high affinity toward other NPs such as Cu, Ag, and Zn (Patel et al. 2018). Consequently, the chelation between the siderophores, augmentation, and dissolution of NPs is expected and promoted. Also, the uptakes of nutrients are exudated often from the insoluble sources of plants (Jones and Darrah 1994). The study conducted by Huang et al. (2017) indicates that the exudation of synthetic roots can promote the Cu^{2+} dissolution rate in the soil system (Huang et al. 2017). The organic matter composition in the rhizophore differs for each plant. Thus, the effects are different in each plant. Judy et al. (2012) conducted experiment on bioavailability of Au NPs in plants and he concluded that the aggregation of Au NPs occurred in *Nicotiana tabacum* and *T. aestivum* and the variation in root exudates affects the plants bioavailability.

The plant tissue and shoots got accumulated by NPs including the newly developed seeds (Rico et al. 2011). The characteristics of plants and NPs play an important role in the translocation of NPs. Au NPs accumulate in the shoots of *O. sativa*, whereas in *Raphanus raphanistrum* and *Cucurbita pepo*, it is not accumulated in shoots (Zhu et al. 2012). In addition, Au NPs with positive charge can be readily taken up by the plant roots. Contrastingly, Au NPs with negative charge are resourcefully translocated into the plant shoots from the roots (Zhu et al. 2012). Among the most commonly studied NPs, TiO_2 and SiO_2 NPs are found in plant tissue of their immaculate speciation (Larue et al. 2011; Servin et al. 2012). The accumulated speciation in plants changes as a result of transformation of NPs such as CuO, La_2O_3, and CeO_2 by disparity. Castillo-Michel et al. (2017) reported the transformation of ZnO NPs during the exposure to plants which are determined by

X-ray absorption spectroscopy (XAS). Zn majorly accumulates in *Z. mays* roots and shoots, where it found in different forms like Zn-phosphate under the hydroponic exposure of ZnO NPs. The translocation of Zn in ionic form has improved the dissolution in rhizosphere. The accumulation of Zn leads to its speciation in the wheat crop (Dimkpa et al. 2012). Although different Zn speciation occurred, there was no ZnO found in shoots when ZnO NPs were exposed to roots. Thus, the transportation and uptake of Zn in the form of Zn^{2+} ions released from ZnO NPs have caused the higher exposure (Lv et al. 2015). The CuO NPs exposure can lead to accumulation of Cu^{2+} ions in *T. aestivum*. It has been reported that CuO in the form of Cu(II) ions formed by reduction of Cu(I) within the plants caused Cu(I)–S complex formation (Dimkpa et al. 2012). Similarly, Cu(II) was reduced to Cu(I) in plants and its observed in the soil cultivated with *Z. mays* and *O. sativa* (Peng et al. 2017). The CuO NPs of 40 nm were transported to shoots and roots in *O. sativa*. The Cu(II) ion was combined mostly with cysteine, phosphate ligands, and citrate, and few are reduced from Cu(I) to Cu_2O.

The CeO_2 and ZnO NPs were translocated from soil in *G. max*. The translocated CeO_2 reveals the form of NPs and Zn biotransformed into Zn–citrus inside the tissue of plant (Hernandez-Viezcas et al. 2013). Table 1 gives the summary of NP's accumulation in crop plants.

1.3.3 Oxidative Stress Responses

1.3.3.1 Enzyme Assays

Several responses are included against environmental stress in the defensive systems of plants at biomolecular level. The oxidative stress enzymes were synthesized, such as peroxidases, catalase (CAT), malondialdehyde (MDA), SOD, and a range of glycoproteins in response to the environmental stress (de la Rosa et al. 2017). MDA is produced when peroxidation of polyunsaturated fatty acids occurs with free radical which is a biomarker of oxidative stress (Placer et al. 1966). In Cilantro plants, CAT increases when exposed to 0–500 mg kg^{-1} of $nCeO_2$ in soil and $nCeO_2$ of 62.5 and 125 mg/kg, the accumulation caused increase of ascorbate peroxidase activity. The increase of CAT activity causes elongation in plants which is correlated with cellular activity increase and production of H_2O_2 (Morales et al. 2013). The impact of exposure of nano-Fe (5 ng–50 mg) in *Physcomitrella patens was investigated* for 7 days and no impact was observed on reactive nitrogen species, and reactive oxidative species. The production of MDA and regulation of glutathione were determined through the negative effects (Canivet et al. 2015). The catalytic interaction between plants and NPs is confirmed by the enzyme activity which demonstrates the hermetic effect in plants. The dose response activity is defined in plants by hormesis effect in which the lower doses induce beneficial effect and higher doses cause inhibitory effect (Calabrese and Blain 2009). The membrane leakage, MDA (lipid peroxidation), and H_2O_2 measurements prove to be a successful indicator of oxidative stress assessment in plants.

Table 1 Accumulation of different NPs in the root part of various crops

NPs	Concentration (mg/L × mg/kg)	Crops	Accumulation in root (mg/kg)	References
ZnO	1000	*Z. mays*	10	Lv et al. (2015)
	100	*S. lycopersicum*	—	Raliya et al. (2015)
TiO_2	100	*T. aestivum*	110	Larue et al. (2012)
	1000	*S. lycopersicum*	—	Raliya et al. (2015)
$Mg(OH)_2$	1000	*Z. mays*	1000	Shinde et al. (2020)
Ag based	250	*Solanum lycopersicum*	—	Adisa et al. (2020)
	1000	*O. sativa*	20	Thuesombat et al. (2014)
	4000	*Glycine max*	2102	Hernandez-Viezcas et al. (2013)
	418.4	*L. sativa*	—	Doolette et al. (2015)
Cu based	100	*Oryza sativa*	9000	Peng et al. (2015)
	500	*B. juncea*	>500	Nair and Chung (2015)
	20	*Lactuca sativa*	9941.3	Hong et al. (2015)
	1000	*Ipt-cotton*	7000	Le Van et al. (2016)
	125	*Vigna radiata*	—	Dimkpa et al. (2012)
	100	*Phaseolus vulgaris*	800	Apodaca et al. (2017)
	20	*Cajanus cajan*	5.82	Shende et al. (2017)
	1000	*Cucumis sativus*	500	Kim et al. (2013)

1.3.3.2 Omics

The metabolomics (metabolite profiles of a unit), genomics (structure and function of DNA), transcriptomics (mRNA study), and proteomics (structure and study of proteins) are the omics-based approaches in biology which are well-known (Espín-Pérez et al. 2014).

The literature suggests that these analytical methods are good oxidative stress indicators in ENMs–plant exposure studies (Ruotolo et al. 2018). Majumdar et al. (2015) performed proteomic analysis in *P. vulgaris* seeds where the plants cultivated by embedding CeO_2 NPs. There is an up-regulation of stress-related to proteins in plants and seeds which are exposed to 125 and 62 mg/kg. The exposure of CeO_2 NPs showed similar results when applied via foliar route (Salehi et al. 2018). The effects of ENMs in plants were explored using proteomics and genomics. Rice plants exposed to TiO_2 NPs were analyzed using gas chromatography and mass spectroscopy which revealed that the amino acids level and palmitic acids in grains have increased due to its exposure (Zahra et al. 2017). The results observed were similar when *Cucumis sativus* plants exposed with CuO NPs. The metabolomics approaches based on NMR and GC–MS have reported an alteration in fatty acid metabolites, sugars, and amino acids (Zhao et al. 2012a, b). The results suggest that ENM's exposure affected the fatty acids and amino acids. Few studies have used omics techniques, where the prematuration can be concluded only through the effects of specific ENM in several plant species. The complexities in omics-based approach is the data handling, instrumentation, and sample handling.

2 NPs Toxic Effects on Human Health

The extensive usage and production of NMs have raised many concerns to human's health based on their potential toxicity, life cycle, and fate (Khan et al. 2010). The indispensable research are the soil contaminants and their sources were identified which are in close association with human health (Khan et al. 2010; Rai et al. 2018). The applications of nanotechnology in various sectors are environment, agriculture, energy, and medicine (Rai et al. 2018; Xiong et al. 2017). The nano-toxicity of the food crops should be considered because of its adverse and harmful effects on human health and physiology of crops (Xiong et al. 2017). The interaction of NPs with the human is a critical subject which necessitates its determinations. The stress reactions are activated by ingestion and destruction of foreign matters by the phagocytes. These can lead to weakness as well as inflammation against the other pathogens in the body defense. In addition, the exposure of NPs to fluids and tissues can take up more macromolecules on the surface which will affect the regulation of enzymes and proteins. The NP toxicity is highly complicated to simplify apropos the health risk associated with the exposure of NPs. The human body has developed tolerance against naturally occurring molecules and elements. Figure 3 shows the natural pathways of NP exposure with affected organs and its associated diseases.

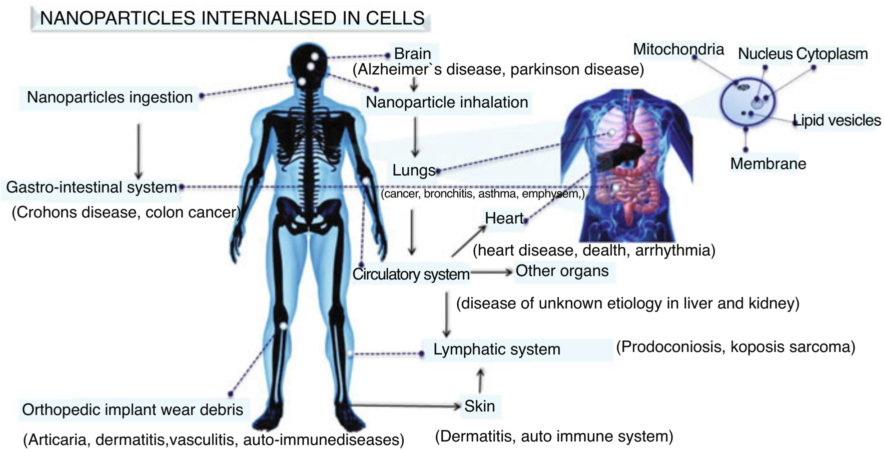

Fig. 3 Natural pathways of exposure of NPs with affected organs and associated diseases

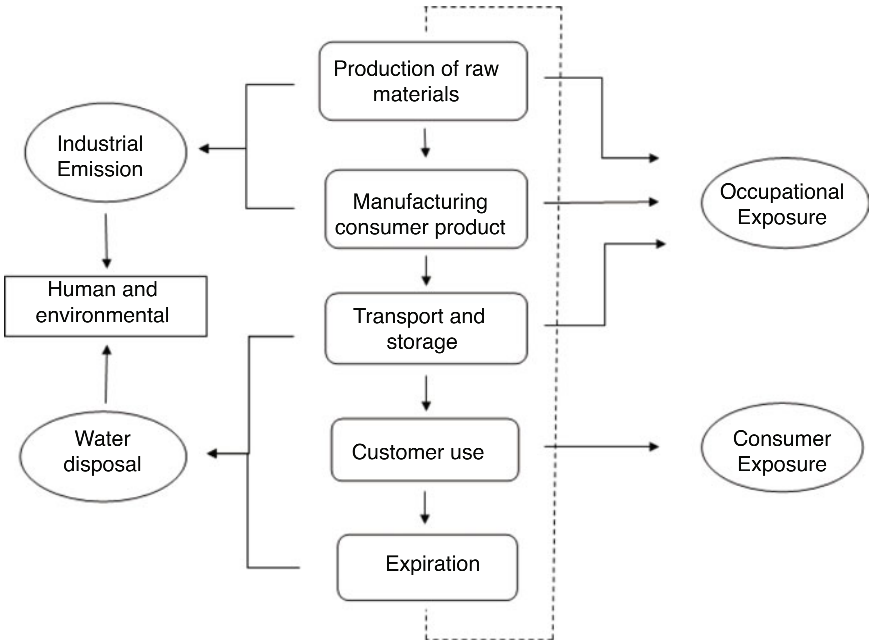

Fig. 4 Flow chart of sources of occupational and consumer exposure

The exposure of NPs to human can be categorized as (1) inhalation from workplaces, (2) dermal route through usage of cosmetics, (3) ingestion which includes food products containing the NPs, and (4) injection such as medical nanotechnology. The NPs can enter into the body through skin, lungs, and digestion systems, where it facilitates free radicals generation that damages the cell. When NPs are in blood stream, NPs become competent for traverse into the blood–brain barrier (Thomas et al. 2013). The toxicological effects of NPs were investigated during the products life cycle which includes usage, disposal, and production. Hence, the hazardous impacts on human health and the food chain can be restricted. The possible pathway of occupational, environmental, and human exposure to ENMs is shown in Fig. 4.

The three most significant causes of toxicity of NPs on living cells are (1) the chemical toxicity occurred from the material and it is made such as the release of Cd^{2+} from CdSe NPs. (2) The small size of NPs can make it stick to the cell membrane and enters into the cell. The attachment of NPs to the membrane and NPs storage can damage function of cells even if the NPs are inert, where it will not react and decompose with the matrix of the components. (3) Depends on the NP's shape.

The NPs enetering into the body through various routes possess severe toxicity. The NPs passage into the soil, air, and aquatic systems are reported by Gupta and Xie (2018).

The NPs contact with the environment and human beings can be dangerous. Few research have shown that consumption of TiO_2 NPs of size 20 nm and Fe NPs causes lung damage to rats (Fraser et al. 2011; Gonzalez et al. 2008). Also, fullerene and TiO_2 can cause brain damage in dogs and fish (Shaw and Handy 2011). Ag and TiO_2 NPs have demonstrated genotoxic and cytotoxic effects to mice cells and human cells because of the generation of reactive oxidative species which causes DNA damage and cell proliferations (Mohamed and Hussien 2016; Wan et al. 2012). The toxicological effects of ZnO and CuO NPs through the plant system on human health were demonstrated by Rajput et al. (2018a).

3 Toxic Impacts in Aquatic Systems

The rapid increase in the usage of ENMs in industrial, agriculture, and consumer products elevates the ENM's production globally. The quick increase in the use of the ENMs can lead to its release into the environment, particularly in the aquatic environment. The discharge of ENMs directly from sewages, river influx, and effluents or indirectly from aerial deposition, run-off, and dumping discharges leads to the movement of ENMs into different ecosystems, such as in water, biota, and sediments (Rocha et al. 2015). In the aquatic systems, the behavior and fate of ENMs are dependent on the property, such as size, shape, charge, particle size, chemical composition, shape, and solubility which are the important characteristics for explaining the stability, bioavailability, reactivity, and homogeneity in different media of ENMs (Kahru and Dubourguier 2010). The transport of ENMs in the water can help to interact with the organisms easily. When the size increased by the process of agglomeration, they become less mobile and tend to deposit to the sediments which becomes less available to the aquatic organism in water column, but it is available more for benthic organisms and deposit feeders (Freixa et al. 2018). Due to the particulates settling behavior, the benthic organisms are exposed more likely (Selck et al. 2016). A review reported by Minetto et al. (2016) points out an important asymmetry that is almost 76% of the papers published are related to ENM's behavior in freshwater animal species, whereas 24% are marine species making it to be highly difficult to understand the possible interactions with inhabiting organism of marine environments. Table 2 shows the predicted environmental concentrations (PECs) of highly produced and used nanoparticles in different major pathways in the environment.

Therefore, the toxic effects toward the microorganisms by ENMs depend mainly on the NM behavior and also the physical and chemical characteristics in the aquatic systems. Also, the toxicological effects are depended mainly on the uptake of ENMs by the aquatic organisms. The different behaviors of the NPs were observed by Ward and Kach (2009) when fluorescent polystyrene NPs of 100 nm delivered to *C. virginica* and *Mytilus edulis*, where the long retention time was induced in the aggregates which indicates the NP transfer from gut to digestive gland and the crucial role of suspended matter. The following sections deal with the knowledge

Table 2 Predicted environmental concentrations (PECs) of highly produced and used nanoparticles in different major pathways in the environment

Nanoparticles	Predicted environmental Conc.	Pathway into the environment	References
Ag-NPs	0.088–10,000 ng L^{-1}	Surface water	Kim et al. (2013)
	0.0164–17 ng L^{-1}	Waste water treatment effluent	Kim et al. (2013)
	0–0.6 pg/L	Sea water	Garner et al. (2017)
CNTs	3.69–32.6 ng L^{-1}	Waste water treatment effluent	Kim et al. (2013)
	0.02–0.2 pg L^{-1}	Seawater	Garner et al. (2017)
	0.003 ng L^{-1}	Surface water	Kim et al. (2013)
Au NPs	100,000 ng L^{-1}	Surface water	Kim et al. (2013)
CeO_2-NP	0.00–0.001 ng/L	Sea water	Gottschalk et al. (2015)
	10^{-12}, 10^{-11} kg/m^3	Surface water	Maurer-Johnes et al. (2013)
	0.03 pg/L		Garner et al. (2017)
Fullerene	0.003 ng/L		Kim et al. (2013)

of ENMs that are hazards, selected based on the published list of ENMs by OECD WPMN (OECD 2010). The ENMs selected are: (1) silver, (2) gold, (3) cerium dioxide, (4) titanium dioxide, (5) carbon nanotubes, and (6) fullerene. Table 3 shows the effects of different NPs on bivalve species.

3.1 Metal-Based Nanomaterials

3.1.1 Ag NPs

3.1.1.1 Characteristics

Ag NPs hold small-to-numerous number of metal atoms which are stabilized by surfactant, polymers or dendrimers and ligands (Beyene et al. 2017). The size of Ag NPs ranges from 1 to 100 nm in diameter (Behra et al. 2013). The spherical Ag NPs are used most commonly and the well-known form of Ag NPs is thin sheets, diamond, and octagonal. The distinct physiochemical properties of Ag NPs are thermal conductivity and high electrical property, catalytic activity, SERS, and chemical stability (Tran and Le 2013).

Table 3 Effects of different NPs on bivalves species

NPs	Concentration	Bivalves time	Species	Tissues	Effects
Ag	10 mg L^{-1}	7 days	Mussels *Mytilus*	G, DG	Increased DNA damage
				LPO	Increased SOD, CAT and
	0.7 mg L^{-1}	3 h	Mussels *Mytilus*	O, DG	Increased accumulation of Ag
	10 μg L^{-1}	14 days	Clams *Scrobicularia*	O	Increased accumulation
	0.2 mg L^{-1}			H_2, O	Decreased phagocytosis in hemolymph
Au	2 mg L^{-1}	180 h	Clams *Corbicula*	O	Subsurface transfer of NPs via Bio deposition
	100 μg L^{-1}	16 days	Clams *Scrobicularia*	O, DG	Increased DNA strand breaks and genetic damage
	6–30 mg L^{-1}	28 days	Clams *Ruditapes philippinarum*	O, DG, G, F	Increase SOD; CAT; GSTs accumulation of Au-NPs increases
	0.1, 1 mg L^{-1}	14 days	Clams *Ruditapes decussatus*	O	Increase SOD; CAT; GST; MDA
TiO_2	0.1, 1 and 10 mg L^{-1}	96 h	Clams *Tegillarca granosa*	G	Increase neurotransmitters; decrease AChE
	0, 2.5 and 10 mg L^{-1}	14 days	Mussels *Mytilus coruscus*	H	Increase hemocyte count; increased hemocyte mortality
	1, 10 μg L^{-1}	30 min	*Clams Ruditapes philippinarum*	H	Phagocytic activity
	1, 10 and 100 μg L^{-1}	14 days	Mussels *Mytilus galloprovincialis*	DG, H	Increase CAT; decrease lysosome membrane stability
ZnO	0.1–2 mg/L	12 weeks	*Mytilus galloprovincailis*	O	Increase respiration rate; increase ZnO accumulation
	1, 5, 10 μg L^{-1}	4 h	Mussels *Mytilus*	H^+	Increase ROS production
					Decrease lysosome membrane stability
	3 mg kg^{-1}	2 weeks	*Scrobicularia plana*	O	Increase oxidative stress
	4 mg L^{-1}	48 h	Oysters *Crassostrea gigas*	G, DG	Increase ZnO accumulation
					Increase LPO; GPs
CeO_2	100 μg L^{-1}	6 days	Clams *Corbicula fluminea*	O	Increase DNA damage
					Increase LDH
	1 and 10 mg L^{-1}	96 h	Mussels *Mytilus galloprovincialis*	O, G	Increase concentration of CeO_2 NPs resulted
	3–30 mg L^{-1}	8 days	Mussels *Mytilus galloprovincialis*	O	Increase concentration of CeO_2 NPs resulted
	1, 10, 50 mg L^{-1}	30 min	Mussels *Mytilus galloprovincialis*	H	Decrease lysosome membrane stability; decrease phagocytic activity

3.1.1.2 Applications

Ag NPs utilize 313 products according to PEN (project on emerging nanotechnologies) which corresponds to 24% of the listed product by Tran and Le (2013). Various applications of Ag NPs are industrial, cosmetics, healthcare-related and household products, antimicrobial agents, and optical sensors, and also as anti-cancer drugs (Balasurya et al. 2020; Janani et al. 2020; Kokilavani et al. 2020; Korani et al. 2015). It is also used frequently in keyboards, biomedical devices, textiles, wound dressings, and water purification systems (Li et al. 2014; Sondi and Salopek-Sondi 2004; Broglie et al. 2015).

3.1.1.3 Toxic Effects of ENMs

Ag NPs change the permeability of cell membrane to K^+ and Na^+ ions which affects the ATP, or mitochondrial activity (Kone et al. 1988). The reported literatures have proven that the toxic effects on cytokine expression by human peripheral blood mononuclear cells and proliferations are induced by Ag NPs (Shin et al. 2007). Severe toxic effects on reproductive systems are shown by Ag NP's exposure (Auffan et al. 2009). The sperm cells were affected adversely, where the materials deposited by crossing the blood–testes barrier. The release of Ag^+ ions and ROS generation is a more relevant factor which strongly indicates the Ag NPs toxicity (Molleman and Hiemstra 2015). The toxicity of Ag NPs increased under UV radiation when compared to dark, where it can accelerate the release of Ag^+ ions and generation of ROS (Zhang et al. 2018). In aquatic environments, the interaction of Ag NPs with invertebrates is through different numbers of biological surfaces such as skin, gut tissues or gills, and cell wall (Zhang et al. 2018).

In bivalves, Ag NPs of 10 mg/L concentration shows damage in hemocyte and accumulation in the mussels *M. galloprovincialis* (Gomes et al. 2013). The same authors have performed another study by exposing Ag NPs to mussel species for the measurement of metal accumulation and as a biomarker for oxidative stress (Gomes et al. 2013). In digestive glands and gills, Ag^+ ions and Ag NPs were accumulated. Ag NPs and Ag^+ ions activate the anti-oxidant enzymes, such as catalase, glutathione peroxidase, and superoxide dismutase. The direct accumulation of Ag has induced metallothionein in gills, but in the digestive glands, it is found that only small Ag fraction is associated with protein. The gills exposed to Ag NPs have caused higher lipid peroxidation, where Ag^+ ions caused lipid peroxidation in digestive glands. Zuykov et al. (2011) provided new information that Ag NPs circulate internally in bivalves. Ag NPs penetrate the hemolymph demonstrated by the authors specifically by radiolabeled Ag NPs of size more than 40 nm and 0.7 mg/L, where the accumulation in the soft tissues is 60% in mussels *M. edulis* with higher concentration in the digestive organs and 7% of accumulation was found in extrapallial fluids. In *M. edulis*, the shell nacre micromorphology of juveniles and adults was examined by Zuykov et al. (2011). However, Ag exposed after depuration to the nacreous layer of adults and young, where there is no evidence found for alteration processes and carobonate particles in grain forms on the nacre tablets. The toxic effect was not always found in bivalves exposed to Ag NPs. In deposit-feeder calm case, Ag NPs in different forms such as aqueous ions, micrometer-sized, and nanoparticles at a concentration of 150–200 microgram per gram were tested. In the tested concentrations, there were no effects on burrowing behavior, mortality, and condition index in all the experiments performed (Dai et al. 2013). The effect and uptake of Ag NPs (40 nm size of 10 μg/L) on clam species *Scrobicularia plana* were examined by Buffet et al. (2013) which were exposed directly to water contaminants or through diet to microalgae. To assess the effect on behavioral changes and reproductive system in animals, the effect on anti-oxidants activity such as glutathione peroxidase, superoxide dismutase, glutathione-S-transferase, and catalase, and effects on intracellular levels of ROS were examined when Ag NPs of 0–500 μg/L were exposed to animals. Furthermore, the activity of sodium–potassium triphosphate was explored. Moreover, the ATPase activity was inhibited to 82.6% at concentration of 500 μg/L. The toxicity on oysters embryonic development was characterized by Ringwood et al. (2009) and relative sensitivity was compared for embryos and adults of oysters *C. virginica* on exposure of 16–0.0016 μg/L. The adverse effects on development of embryo were observed at Ag NPs' concentration of 0.16 μg/L and also the lysosome of adults was destabilized. In both adult and embryo oysters, there is a significant increase on the metallothionein mRNA levels and particularly in embryo, the metallothionein levels were elevated. However, authors cannot identify whether the cause for gene expression and toxicity is Ag^+ ions dissociated from the NPs or Ag NPs (Ringwood et al. 2009). The citrate-capped Ag NPs of 20–30 nm have increased the level of proteins in the same species and further it causes greater oxidative damage to hapatopancreas (McCarthy et al. 2013). The result reveals the Ag NP's uptake and transport to the hepatopancreas in situ. Ag NPs of 26 nm from 1 to 400 mg/L concentration were exposed in which the phagocytosis was significantly decreased in the *C. virginica* when comparing it with the control and it differed very little in Ag NPs and Ag^+ ions (Chalew et al. 2012).

3.1.2 Au NPs

3.1.2.1 Characteristics

Au NPs are studied extensively as it is the key materials in nanotechnology and nanoscience (Zhou et al. 2009). The range of its applications is extended widely because of its versatile surface chemistry and spherical morphology allowing them to be coated with polymers, biological recognition molecules, and smaller molecules (Li et al. 2013). Au NPs of spherical shaped possess optical property which differs in its aggregated states due to electron oscillation at its surface and the properties are fine-tuned by controlling its size, sharpness, chemistry, and composition (Chen et al. 2018). Au NPs serve to be an excellent scaffold for immobilizing specific functional groups in large quantities which lead to high sensitivity and rapid responses for targeting the analyte because of its high surface area-to-volume ratio (Yeh et al. 2012). They also exhibit good compatibility with almost biologically and chemically active molecules (Chen 2018).

3.1.2.2 Applications

Au NPs are of great interest in various fields due to its unique properties. Their wide range of applications are drug delivery, therapeutic agents, sensory probes, electronic conductors, organic photovoltaics, and catalysis. Also, it is used widely as anti-fungal, anti-microbial, and anti-biotic agents and it is used in coatings, plastics, textile, nanofibers, therapeutic drug delivery, sensor devices, electronic chips, and catalytic applications (Yeh et al. 2012).

3.1.2.3 Toxic Effects of ENMs

Au NPs attribute to the interaction of cell membrane that causes oxidative stress leading to cytotoxicity, and metabolomic activity inhibition which leads to mitochondrial and nuclear condensed DNA damage (Goodman et al. 2004). The toxicity of Au NPs is associated with ROS generation which is connected to the catalytic property of Au NPs. The Au NP's ecotoxicity in bivalves shows that NP's uptake and accumulation cause unexpected biological responses (Canesi et al. 2014). The exposure of Au–citrate NPs of 5.3 nm to *M. edulis* causes oxidative stress condition and the accumulation of Au NPs was found to be much higher in both gills and digestive glands. It shows that Au could specifically cause induction of higher ubiquitination in both gills and digestive glands (Tedesco et al. 2010). Also, Au NPs of 95% were accumulated in digestive glands which cause lipid peroxidation and decrease in thiol containing proteins and the exposure causes decrease in LMS in the hemocytes (Tedesco et al. 2010). In *M. galloprovincialis*, the four metal NPs were selected by the different physiochemical characteristics for screening it cytotoxicity in hemocytes and gills with different Au NP's concentrations (0.1, 1, 10, 25, 50, and 100 mg/L). The toxicity was low in mussel hemocytes by bulk Au and Au NPs. The most toxic form of Au was in ionic form which causes decreased hemocyte viability from 25 mg/L. From 50 mg/L, Au NPs of three sizes decreased the hemocyte viability. (5, 15, and 40 nm) (Katsumiti et al. 2016). At 50 mg/L, Au^{3+} ion concentration and Au NPs of 6 mg/L and 30 mg/L accumulated in both gills and digestive glands (Garcia-Negrete et al. 2013) of calm species *R. philippinarum*. Au NPs internalization was also studied and investigated thoroughly in the early stages of oyster *C. gigas*.

3.1.3 TiO_2 NPs

3.1.3.1 Characteristics

TiO_2 exists in different polymorphs, such as brookite, anatase, and rutile. The most stable form of it is rutile. The common oxidation states of Ti are +2, +3, +4, and +6. Due to the oxygen deficiency in TiO_2, it is said to be an n-type semiconductor (Wisitsoraat et al. 2009; Asahi et al. 2000). TiO_2 investigated widely as a photocatalyst because of its high photo-activity, thermal stability, low toxicity, low cost, and good chemical stability (Hoffmann et al. 1995). Many undesired compounds are mineralized using TiO_2. Also, TiO_2 absorbs UV radiation for the generation of reactive oxidative species which can damage the DNA substantially (Dunford et al. 1997; Hidaka et al. 1997).

3.1.3.2 Applications

Various applications of TiO_2 NPs include electronics, medicine, cosmetics, environmental remediation, and innovative food products. TiO_2 used in food products, coatings, pharmaceuticals, papers, toothpaste, medicines, paints, cosmetics, inks, and plastics (Kaida et al. 2004; Wang et al. 2007). It is also used as a pigment for whitening the skim milk. TiO_2 used extensively in sunscreen, because it is considered to be a safe physical sunscreen agent, where it reflects and scatters UVB and UVA which causes skin cancer (Trouiller et al. 2009). In addition, in articulating prosthetic implants, TiO_2 is used for a long time (Jacobs et al. 1991). TiO_2 as a semiconductor photocatalyst can be used for the treatment of contaminated water which is by-products of hazardous industry (Wigginton et al. 2007). The photocatalytic effects of TiO_2 NPs are utilized in industries for several applications mainly for anti-fogging and self-cleaning purposes, such as anti-fogging car mirrors, self-cleaning windows, self-cleaning textiles, and self-cleaning tiles (Robichaud et al. 2009). TiO_2 NPs in nanomedicine fields have been investigated and are said as useful tools for nanotherapeutics and advanced medicines. In addition, TiO_2 NPs possess unique physical properties and it is used ideally in anti-microbial applications and many skin care products (Kaegi et al. 2008).

3.1.3.3 Toxic Effects of ENMs

The physiochemical properties that affect the parameters of the particles are shape, surface characteristics, inner structure, and size. The increase in surface area decreases the TiO_2 NP's size and it increases the harmful effects on human health which are of great concern by the researchers (Andersson et al. 2011). TiO_2 NP's activity is influenced by modification of its surface by coating (Tedja et al. 2012). The cytotoxicity was diminished due to the surface-modified TiO_2 NPs by a polymer-grafting technique in combination with catalytic chain process (Saber et al. 2012).

The effects of TiO_2 NPs on marine bivalves have become issues of major concern (Wang et al. 2014). Doyle et al. (2015) ingested bivalves with TiO_2 NPs and they observed the TiO_2 NPs accumulation and toxicity targets to the gills and digestive glands on *M. galloprovincialis* (Canesi et al. 2012). The NMs reach higher trophic levels from marine bivalves through biomagnification (Wang et al. 2014). Furthermore, the studies have reported that TiO_2 NPs cause oxidative damages in mussels with confirmed increase in catalase activity (Barmo et al. 2013). The toxicity of TiO_2 NPs is not known fully as though there are evident that ROS is generated under UV or visible light exposure (Dalai et al. 2013; Konaka et al. 2001). Sureda et al. (2018) exposed TiO_2 NPs on *M. galloproviancialis* for 24 h in the form of sunscreen. The results showed the increase of metallothionein content. At low sunscreen concentration, the antioxidant and activity of the enzyme glutathione S-transferases were detoxified which showed an increased activity possessing a bell-shaped profile. It was not induced in higher sunscreen concentration. According to the enzyme activity, the malondialdehyde levels are lipid peroxidation marker, where the enzyme level elevates at high concentration of TiO_2 NP. The acetylcholinesterase activity was found to decrease at a higher sunscreen concentration containing TiO_2. D'Agata et al. (2014) exposed TiO_2 NPs (10 mg/L) for 7 days on *M. galloprovincialis*. The mussel tissue was analyzed by ICPES analysis and the results shows that Ti accumulation is tenfold higher in the digestive gland when comparing it with the gills. The accumulation of nano-sized TiO_2 is much greater than bulk mostly in digestive gland that is higher by sixfold. The histology, metallothionein gene expression, and the histochemical analysis reveal that more toxicity caused due to the bulk material. The DNA damage increased significantly in the hemocytes which was determined by the comet assay. Also, the mussels exposed with different TiO_2 NP concentrations of 1, 10, and 100 μg/L caused severe damages (Barmo et al. 2013).

3.1.4 ZnO NPs

3.1.4.1 Characteristics

ZnO NPs possess hexagonal structure and the structure has alternating planes which are composed of O^{2-} and Zn^{2+} ions coordinated tetrahedrally. ZnO NPs possess high surface area-to-volume ratio, long life span, polar surfaces, and high UV absorption (Nolan et al. 2009).

ZnO heterostructure properties were investigated which are essential for the development of nanoscale devices based on the physical properties which includes the chemical sensing, optical, mechanical, electrical, magnetic, and piezoelectric properties (Applerot et al. 2009; Emamifar and Mohammadizadeh 2015). The effects of ZnO on the anti-microbial and mechanical property were studied by Li and Wu (2003) on polyurethane (PU) films. The low-density polyethylene (LDPE) film's anti-microbial activity was tested by incorporating the LDPE along with ZnO NPs in orange juice (Emamifar and Mohammadizadeh 2015).

3.1.4.2 Applications

On large scale, ZnO NPs are used in cosmetic, pigments, anti-virus agent in coatings and in sunscreens (Chen and Lia 2003; Hu et al. 2003; Li et al. 2013) and in tires or polymers were used as stabilizers. The surface-coated ZnO are used in MRI (magnetic resonance imaging) (Xue et al. 2010) and specific delivery of desired drug by magnetic NPs (Fujishima and Honda 1972; Frank and Bard 1977). Ceramic nanoparticulates such as ZnO NPs grow rapidly with wide range of applications, such as polishing, polymer additives, and gas sensor (Lin et al. 1998), catalysis, and medical materials (Nolan et al. 2009).

3.1.4.3 Toxic Effects of ENMs

The relationship between oxyradical production and concentration of ZnO NPs has been studied and ZnO interaction with subcellular compartments can induce the production of n-oxidase which are found to be dose dependent (Miller et al. 2015; Manzo et al. 2013). The study on clam *R. philippinarum* and mussels *M. galloprovincialis* showed toxic effects when exposed with ZnO in calm and mussels on hemocytes and gill cells (Katsumiti et al. 2016). The study performed on *S. plana* reveals that the quanity of Zn of 5.4 μg was accumulated with the exposure of 3 mg of Zn (Buffet et al. 2013). The anti-oxidants were activated which indeed reduced the feeding and burrowing activities. The bivalve *S. plana* shows an increase in oxidative stress when 3 mg of ZnO was sedimented (Devin et al. 2017). The ZnO NPs of 4 mg/L were exposed to *C. gagas* for 24 and 48 h, and the accumulation was 49% and 80%, respectively, which indicates that the accumulation is time dependent (Trevisan et al. 2014). Due to the exposure of both Zn ions and ZnO NPs, the morphology of gills become irregular which led to mitochondrial cristae loss and the digestive glands were damaged as revealed by histopathological analysis. ZnO NPs of concentration of 1–10 mg/L were exposed for 96 h and the uptake of Zn was investigated by Montes et al. (2012). The accumulated amount of Zn is 21% in mussels and pseudo-faces with concentration of 63 μg/L, where the threshold for Zn has saturated.

3.2 Carbon-Based Nanomaterials

3.2.1 Fullerenes

3.2.1.1 Characteristics

Fullerenes are also known as geodesic dome in which the C molecules are arranged in the shape of sphere. Based on the C atoms number, fullerenes exists in multiple configurations, that is, C_{60}, C_{70}, and C_{80}. The buckminsterfullerene with a molecular formula of C_{60}, which is more prevalent in scientific interest terms, production, and aquatic organisms are engaged in research (Petersen and Henry 2012; Britto et al. 2015). The buckminsterfullerene composed of 60 carbon atoms which are in polyhedral form in the hexagon and pentagon configurations. The unique properties exhibited by C_{60} molecule which includes the specific morphology, small size, high electrochemical stability, and well-ordered structure because of the structural characteristics of C_{60}. The specific morphology of fullerene makes it unique when compared with the traditionally used carbon ENMs and such properties include good mechanical properties, special electroconductivity, and good thermal conductivity (Coro et al. 2016).

3.2.1.2 Applications

The various applications of C_{60} are adsorption electrodes (Noked et al. 2011), printing technologies (Dzwilewski et al. 2009), solar cells (Brabec et al. 1999), biosensors (Gavalas and Chaniotakis 2000) and electronic applications such as in microwave, and mobile telephones (Coro et al. 2016) and many number of products are exploited.

3.2.1.3 Toxic Effects of ENMs

Fullerene C_{60} caused toxic impacts in the organisms by inducing oxidative stress (Usenko et al. 2008). Fullerene generates ROS particularly superoxide and singlet oxygen in the presence of UV and visible light (Kamat et al. 2000) which induces oxidative stress leading to various detrimental downstream effects, including cell death, protein adduction, DNA repair, and lipid peroxidation (Pickering and Wiesner 2005). The shape, size, surface structure, aggregation, and chemical composition of Fullerene C_{60} can modify the binding site of protein, cellular uptake, and cause injury to tissues (Nel et al. 2006). The studies demonstrated that fullerene causes toxic effects on bivalve through biochemical and physiological responses. The exposure of fullerene (1, 5, and 10 μg/L) to *Mytilus galloprovincialis* hemocytes in the form of suspension induces the release of lysozyme, production of extracellular nitric oxide and oxyradicals. The other concentrations of fullerene

(0.05–0.2–1–5 mg/L) were investigated by the same authors which demonstrates that the NMs caused destabilization of digestive gland and hemocyctes. Fullerene induced the accumulation of lysososomal lipofuscin at higher concentrations of C_{60} which increases the anti-oxidant enzyme catalase activity and stimulated glutathione S transferases (Canesi et al. 2014). The exposure of fullerene C_{60} (1.5 and 10 μg/L) was reported to cause cytotoxicity generated through the circulation (Moore et al. 2009). Sanchis et al. (2018) evaluated the metabolic responses when *M. galloprovincialis* exposed to fullerene (10 mg/L). The bioaccumulation was confirmed by these authors when metabolomic of the organism caused a significant difference in free amino acid concentrations when compared with control groups. The glutamine concentrations decreased significantly which suggest that the metabolism of facultative anaerobic energy has been activated. Also, the lipid content has differed significantly which concludes that these results confirm the oxidative stress and hypoxia. The other model species, oyster *Crassostrea virginica* exposed to fullerene, have caused destabilization of lysosomes and embryonal development and the effects of fullerene were dosage depended (1–500 μg/L) (Ringwood et al. 2009). The accumulation of C_{60} fullerene was also found in hepatopancreas cells and lysosomes which conclude that the targeted pathway of fullerene is lysosomal and endocytotic cells.

3.2.2 Carbon Nanotube (CNTs)

3.2.2.1 Characteristics

Nanotubes belong to fullerene structural family including buckyballs. CNTs are cylindrical shaped, and buckyballs are spherical shaped, and it is single walled with <1 nm of diameter or multi-walled carbon nanotubes (MWCNTs) of diameter more than 100 nm which consists of several nanotubes linked concentrically (McEnaney 1999). The length can reach from millimeters to micrometers. The chemical bonding in CNT with sp2 and it allows stronger interaction between the molecules (Baughman et al. 2002).

Various properties of CNTs include that they are highly flexible, high thermal conductivity, high aspect ratio, electrical conductivity, and tensile strength, very high elasticity, which can be considerably bent without damage and low thermal expansion co-efficient (Ajayan and Zhou 2001).

3.2.2.2 Applications

CNT materials are incorporated by the commercial applications. The commercial applications of CNTs at present and future are the most promising one possessing excellent thermal conductivity, conductive properties, energy storage, field emission for molecular electronics, structural applications, air and water filtration, and biomedical applications (De Volder et al. 2013).

3.2.2.3 Toxic effects of ENMs

According to the data available regarding the toxicity of CNT, harmful effects are induced by CNTs, where it can cross the membrane barriers and it can cause inflammatory and fibrotic reactions. The interaction between CNT and cells includes the cellular uptake and the CNTs entered by different routes cause cytokines production, reactive oxidative species, membrane perturbations, and cell apoptosis (Zhao et al. 2012a, b). The CNTs accumulate in various subcellular compartments which include mitochondria (Neves et al. 2010), cell cytosol (Al-Jamal et al. 2011), perinuclear region (Lacerda et al. 2007), endosomes (Antonelli et al. 2010), and nucleus (Shi Kam et al. 2004) in accordance with the functionalization and physiochemical properties. The indirect toxic effects of CNTs which are non-specific include the surface tissue occlusions and physical irritations and it is observed in aquatic organisms (Oberdorster et al. 2006).

At larval stages, the ecotoxicity by CNT was observed in *Xenopus laevis* with physical blockage in the digestive tract and gills and it bioaccumulates in the intestine (Mouchet et al. 2008). Various studies on exposure of CNTs on bivalves have provided the biochemical and physiological responses on bivalves. Also, the toxicity of different CNTs was evaluated by Mwangi et al. (2012), where he noticed the reduction of its growth and survival of mussel *Villosa iris*, but there is no evidence for supporting the CNTs penetration inside the cell membranes.

4 Exposure of ENMs in Atmosphere

ENMs interact with the naturally occurring NPs present in the atmosphere. Airborne viruses and bacteria are nano-organism which interacts by attaching itself to ENMs and making them as disease spreading particles. The atmospheric properties of nanoparticles need to be studied in detail which help us in understanding the residing time in the atmosphere, penetration of the NPs inside the respiratory system, and probability of them being inhaled. ENMs in smaller size behave like vapor, dominate the dispersion, and it diffuses rapidly in the air for longer period.

The Ag, TiO_2, and carbon nanotubes concentrations were estimated by modeling study of exposure of Ag and TiO_2 ENMs in the atmosphere (Mueller and Nowack 2008). Sanchis et al. (2012) studied the effect of fullerene and the results show that the concentration of fullerene bound aerosol was more than the concentration of modeled, which attributes to natural fullerene. The formation of naturally occurring fullerene has been observed in the studies of Heymann et al. (2003).

Several studies have reported the involvement of ENMs that is nano-sized aerosols which cause global radiative forcing in the atmosphere (IPCC 2007). The release of ENMs in the air has also led to the accumulations of ENMs in other environments, such as water and soil. The ecological effects caused by ENMs are an important link for quantitative establishment of ENM release (Aschberger et al.

2011). The applications of ENMs to soil and water exposure is high even if the ENMs are directly deposited on soil or washed out of the atmosphere (Zhang 2003).

The chemical reactions are triggered due to the deposition of NPs in soil which interferes with the ecological process. The plant physiology is affected by the accumulation or deposition of airborne NPs on the surface of plant, where it can penetrate through stomata to enter into the cell (Da Silva et al. 2006). The photosynthesis process is affected due to the reduction in availability of sunlight causing shedding effect. The deposition of nanoparticles which are highly toxic and reactive on crops, where it can enter to the high trophic levels via food chain. Similarly, the paddy yield has been reduced by carbon black, where it particularly makes the wheat crop prone to other pollutants (Wild and Jones 2009).

In the atmosphere, ENM's capping can lead to the addition of various contaminants such as zinc oxide and iron oxide in the atmosphere. Algal growth is promoted due to iron oxide deposition. It is a major problem in sea water which has been reported previously. In the presence of light, the generation of ROS by titanium dioxide affects the microorganisms. Reijnders (2008) observed inflammatory injury and respiratory distress, where it have caused oxidative stress in aquatic organism by TiO_2. Also, carbon nanotubes have caused oxidative injury and act as respiratory toxicant to organisms in water (Smith et al. 2007).

5 Conclusions

The specific properties of ENMs make it undergo various levels of environmental degradation when released into the atmosphere possessing different toxicologically and physiological properties. The results are of different degree causing different or similar health effects. The ENMs released in the atmosphere have been altered, where it is important for assessing the human exposure by understanding the knowledge related to inhalation of toxicity of specific ENM. The fate and behavior of ENMs released into the atmosphere are important for studying the effects on atmospheric environment. The overall exposure has been influenced by various abiotic, soil, and plants. A significant progress has been made in understanding the fate, effects, and sources of ENMs in the environment. According to the data available on the volume of production of ENMs, TiO_2 NPs are considered worldwide as most relevant materials in terms of production more than 10,000 t/a, followed by CNTs, CeO_2 NPs, and ZnO NPs, from the range of 100–1000 t/a and Ag NPs of more than 55 t/a. In aquatic environment, these transformations affects the fate, transport, and toxicity of NPs. The fate of ENMs in environment must be understood for assessing the ecosystem exposure and toxicity in biota. Nanotoxicity in water, soil, and air resources is little difficult for locating due to its nanosize compared with bigger pollutant particulates. The concentration of ENMs at nanomolar level is proven to be toxic for the organisms in aquatic environment. The major findings in the literature are based on the predicted number of realistic exposure scenarios which cause potential hazard to agricultural ecosystems. The toxicity, fate, and transport were affected due to the dynamic transformation in the aquatic environments. Only limited studies are made to understand the fate of ENMs in the environment, even though there is same degree of adverse effects are observed in most of the toxicity studies and large number of the behavior is still unexplored.

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Nanomaterials for Removal of Organophosphorus Pesticides from Wastewater

Elsayed A. Elkhatib and Hala M. Hamadeen

1 Introduction

Pesticides are considered a crucial factor for producing abundance and sustainable agricultural food through pests and diseases control. They are inherently poisonous molecules and have the potential to cause harm to the environment if not used properly. However, Farmers who tend to administer copious amounts of it onto their crops do not view pesticides as a poison, but as nurturing medicine (Shepard 2008). Pesticides have not only been used in agriculture, but also are used in households and industries. Hence, the pesticides definition, according to the environmental protection agency (EPA), is a substance or mixture of substances aimed to prevent, destroy, repel, or mitigate pests (USEPA 2006a).

Pesticides are classified according to their chemical composition to insecticides, fungicides, herbicides, nematocides, and rodenticides (Fig. 1). Organophosphorus pesticides (OPPs) are a class of insecticides pesticides frequently used worldwide for both agricultural and residential applications (Singh and Walker 2010). The OPPs, esters of phosphoric acid, comprise a phosphorous atom attached to oxygen or sulfur atom with double bond and attached to methoxy (–OCH_3) or ethoxy (–OCH_3CH3) groups with single bond (Fig. 2). The OPPs frequently used and widely spread in the environment are parathion; malathion; chlorpyrifos; diazinon; dichlorvos; fenitrothion; tetrachlorvinphos; profenofos; azinphos-methyl; terbufos; Azamethiphos; dimethoate; ethoprophos; temephos; triazophos; omethoate, and monocrotophos (Amiri et al. 2018; Naddafi et al. 2018; Katsikantami et al. 2019; Khedr et al. 2019). The OPP characteristics are presented in Table 1.

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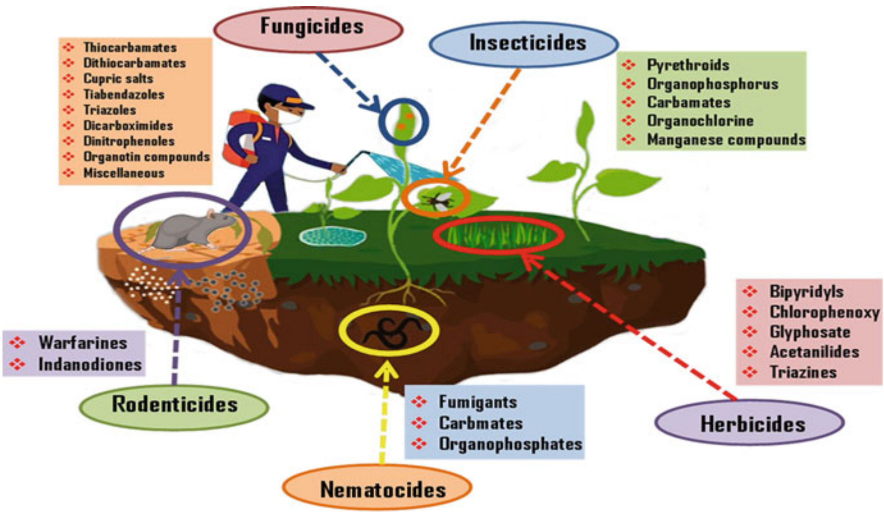


Fig. 1 Classification of pesticide

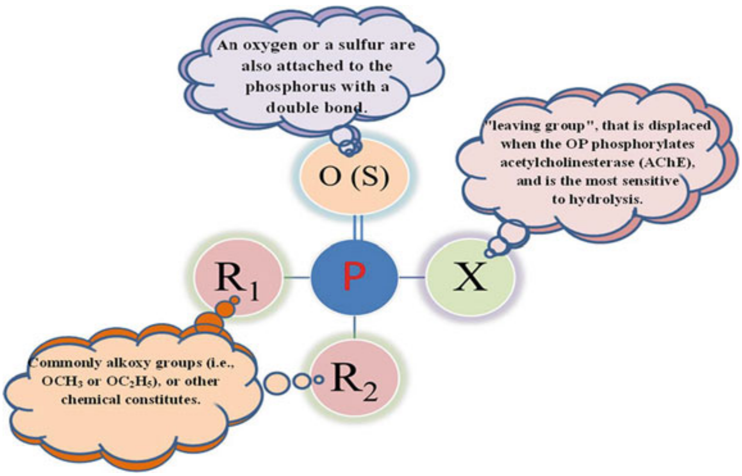
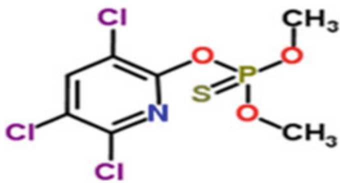
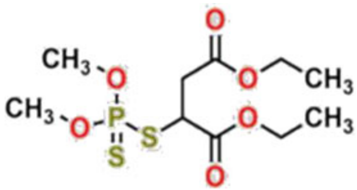
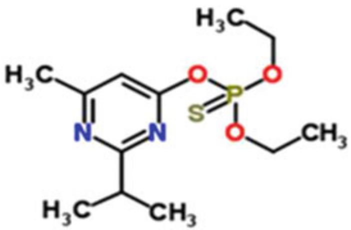


Fig. 2 Chemical structure of OPPs

2 Sources and Occurrence

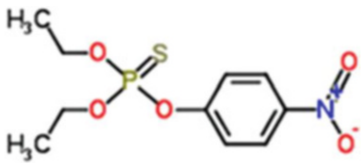
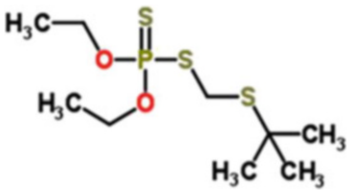
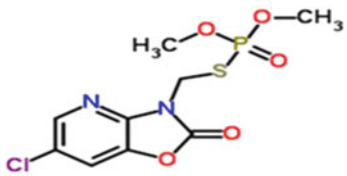
The substantial use of OPPs in agriculture and domestic activities has led to surface and groundwater pollution, either directly by dumping them into the water or indirectly with agricultural, sanitary and industrial drainage water that pour into these surfaces and may reach groundwater (Moussavi et al. 2013). Pesticides exposure, especially the OPPs, occurs mostly through leaching, deposition, surface runoff, and atmospheric transport (Fig. 3). The improper use of pesticides on land

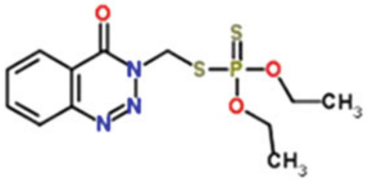
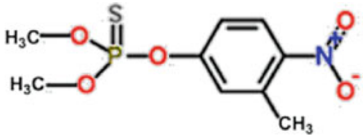
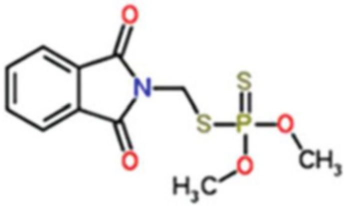
Table 1 Characteristics of organophosphorus pesticides (OPPs)

OPPs	Trade name	Structural formula Chemical name	Chemical formula	MM[a] (g/mol)	SW[b] $mg\ L^{-1}$	[c]Log *Kow*	[d]$T^{1/2}$ water (days)	EPA toxicity	References
Chlorpyrifos (CPF)	Dursban	 Diethyl o-(3,5,6-trichloro-2-pyridyl phosphorothioate	$C_9H_{11}C_{13}NO_3PS$	350.6	2	4.96–5.11	16–35	Class II	US EPA (2011), Mackay et al. (2014), Alizadeh et al. (2018)
Malathion (MLN)	Cythion		$C_{10}H_{19}O_6PS_2$	330.35	145	2.89	17.4 (pH 6)	Class III	Tomlin (2006), US EPA (2009)
Diazinon (DZN)	Spectracide	 Diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate	$C_{12}H_{21}N_2O_3PS$	304.36	40	3.81	138	Class II	Cecchine et al. (2000), US EPA (2006c), NCBI (2015a)

(continued)

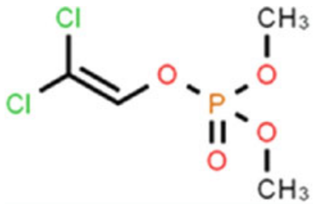
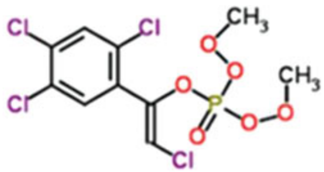
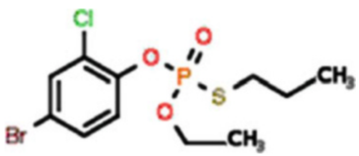
Table 1 (continued)

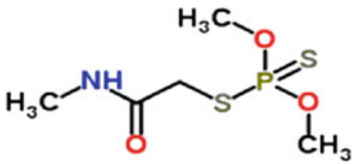
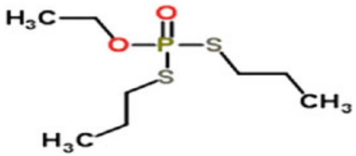
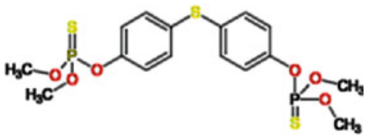
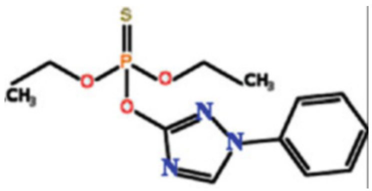
OPPs	Trade name	Structural formula Chemical name	Chemical formula	MM[a] (g/mol)	SW[b] mg L^{-1}	[c]Log *K*ow	[d]$T^{1/2}$ water (days)	EPA toxicity	References
Parathion (PA)	E 605 and Eftol and Folidol	 O,O-diethyl-O-(4-nitrophenyl) phosphorothioate	$C_{10}H_{14}NO_5PS$	291.26	24	3.83	100	Class I	Pope (2014), NCBI (2015b)
Terbufos (TE)	Counter	 S-tert-butylthiomethyl 0,0-diethyl phosphorodithioate	$C_9H_{21}O_2PS_3$	288.42	4.5	4.71	5.5	Class I	Meister et al. (1989)
Azamethiphos (AZA)	Alfacron and Salmosan and Zazafly	 Chloro-2,3-dihydro-2-oxo-1,3-oxazolo [4,5-b]pyridin-3-ylmethyl O,O-dimethyl phosphorothioate	$C_9H_{10}ClN_2O_5PS$	324.68	1100	1.05	10.8 20 °C	Class III	Roth et al. (1993), Cecchine et al. (2000)

Azinphosmethyl (AZM)	Guthion	 Dimethyl-S-([4-oxo-1,2,3-benzotriazin-3 (4H)-yl]methyl)phosphorodithioate	$C_{10}H_{12}N_3O_3PS$	317.32	**30**	2.75	2	Class I	Howard (1991)
Fenitrothion (FN)	Accothion and Agrothion	 O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate	$C_9H_{12}NO_5PS$	277.2	38	3.30	Less than 24 h	Class II	Dikshith (2016)
Phosmet (PMT)	Imidan	 [(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl) methyl]dimethyl phosphorodithioate	$C_{11}H_{12}NO_4PS_2$	317.33	25	2.95	7.8 h	Class II	US Public Health Service (1995)

(continued)

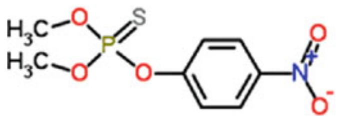
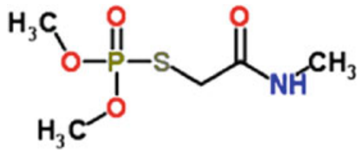
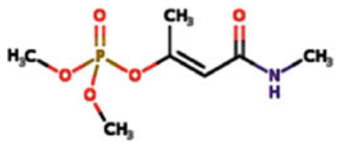
Table 1 (continued)

OPPs	Trade name	Structural formula Chemical name	Chemical formula	MM[a] (g/mol)	SW[b] mg L^{-1}	[c]Log *Kow*	[d]$T^{1/2}$ water (days)	EPA toxicity	References
Dichlorvos (DCV)	Vapona	 Dichlorovinyl dimethyl phosphate	$C_4H_7Cl_2O_4P$	220.98	10,000 18,000	1.9	5.5	Class I	Tomlin (1997)
Tetrachlorvinphos (TCVP)	Gardona	 Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl 6 Tetrachlorvinphos (beta isomer) phosphate]	$C_{10}H_9Cl_4O_4P$	366	11 (20 °C)	3.53		Class III	US EPA (2006b)
Profenofos (PFF)	Curacron	 O-(4-bromo-2-chlorophenyl) O-ethyl S-propyl phosphorothioate	$C_{11}H_{15}BrClO_3PS$	373.63	28	4.44	14.6		Tomlin (1994)

Dimethoate (DMT)	Cygon and Dimate	 Dimethyl *S*-[2-(methylamino)-2-oxoethyl] dithiophosphate	$C_5H_{12}NO_3PS_2$	229.3	23 (20 °C)	0.78–0.79	18 h to 8 weeks	Class II	Jaggi et al. (2011)
Ethoprophos (EPP)	Holdem and Mocap	 Ethyl S,S-dipropyl phosphorodithioate	$C_8H_{19}O_2PS_2$	242.33	750	2.99	25		Robinson et al. (1999)
Temephos (TEM)	Abate	 Thiodi-4,1-phenylene) O,O, tetramethyl phosphorothioate	$C_{16}H_{20}O_6P_2S_3$	466.5	0.03	4.91	>30	Class III	Awadh and Zhao (2016)
Triazophos (TAP)	Hostathion and March and Rider and Spark and Try		$C_{12}H_{16}N_3O_3PS$	313.31	24.7 (20 °C)	3.34	30 to 250		Yalkowsky et al. (2010)

(continued)

Table 1 (continued)

OPPs	Trade name	Structural formula Chemical name	Chemical formula	MM[a] (g/mol)	SW[b] mg L^{-1}	[c]Log *Kow*	[d]$T^{1/2}$ water (days)	EPA toxicity	References
		(O,O-diethyl-O- (1-phenyl-1H-1,2,4-triazol-3-yl) phosphorothioate							
Methyl Parathion (MP)	Dimethyl parathion and Mepaton and Mepatox and Methyl E-605	 (O,O-dimethyl O-4-nitrophenyl phosphorothioate)	$(CH_3O)_2P(S)OC_6H_4NO_2$	263.2	55–60	1.83–3.43	1 month	Class I	Buerger et al. (1994)
Omethoate (OMT)	Folimate and Le-mat and Dimethoxon	 O,O-dimethyl S-methylcarbamoylmethyl phosphorothioate	$C_5H_{12}NO_4PS$	213.19	39.8	−0.74 ((20 °C)	611 h (24 °C)		Awadh and Zhao (2016)
Monocrotophos (MCP)	Nuvacron and Azodrin	 Dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate	$C_7H_{14}NO_5P$	223.16	4.91E +04	−0.22	147	Class I	Ismail and Rao (2000)

[a]Molecular mass
[b]Water solubility at 25 °C
[c]Octanol/water partition coefficient
[d]Half-lives in Water (25 °C and pH 7)

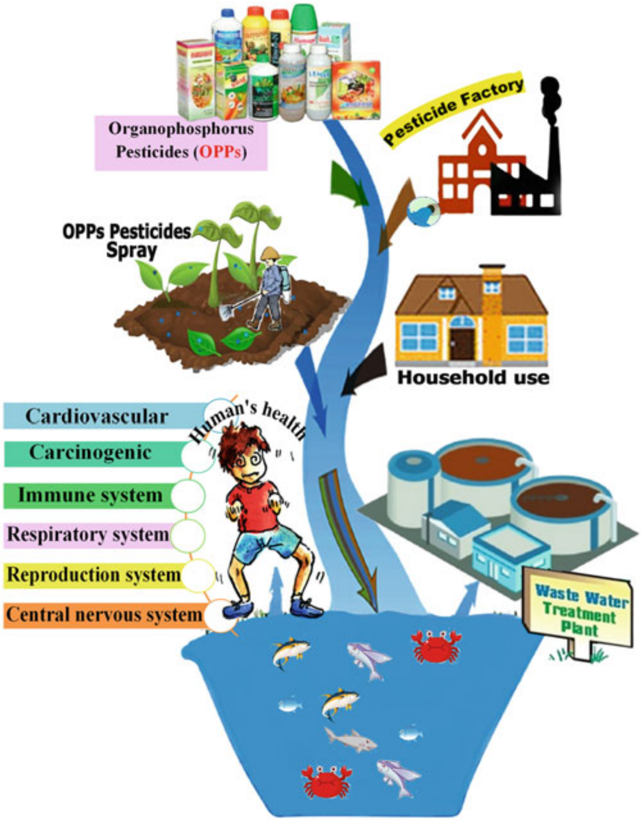


Fig. 3 Sources of OPPs in the environment

ultimately leads to pollution of aquatic environments. Once OPPs enter the aquatic environment, the physical, chemical, or biological conditions of such water bodies will be altered, thereby making it toxic, contaminated, and unsuitable for use (Plakas and Karabelas 2012). Analyses of the samples from contaminated surface and ground water revealed high levels of OPPs such as ethion, parathion-methyl, phorate, chlorpyrifos, and profenofos. The samples from surface water have showed higher levels of OPPs than those from more groundwater (Lari et al. 2014).

The toxicological effects of the OPPs include buildup of acetylcholine in respiratory and cardiovascular systems due to inhibition of acetylcholinesterase (AChE) in target tissues (Coupe et al. 2000; Gupta et al. 2002; Beduk et al. 2012; Moussavi et al. 2013). The European Union (EU) Drinking Water Directives (EEC 1988) have set the maximum OPPs allowable concentration in drinking water to be 0.1 and 0.5 μg/L for individual and total pesticide concentrations, respectively. Thus, OPP compounds, removal from water using effective methods, are important. Currently, various treatment techniques are used for OPPs removal from contaminated water like electrochemistry (Arapoglou et al. 2003; Martínez-Huitle et al. 2008; Samet

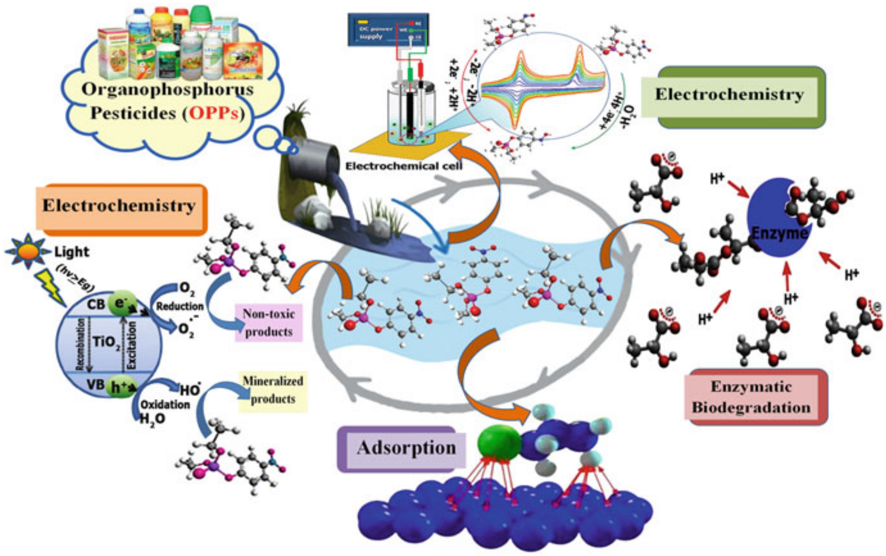


Fig. 4 Treatment processes for the removal of OPPs from aqueous solutions

et al. 2010), adsorption (Li et al. 2005; Johnson et al. 2014), enzymatic biodegradation (Anwar et al. 2009; Cycoń et al. 2013; Wei et al. 2013), and photocatalysis (Fig. 4) (Echavia et al. 2009; Negishi et al. 2012; Hossaini et al. 2014). However, adsorption has become visible to be the most effective and advantageous technique for organic pollutants removal, and developing new green cost-effective adsorbents with high adsorption capacities is urgently needed to overcome the persistent.

3 Nanomaterials

Nanotechnology is the ability to use the extremely small materials in the range of 1–100 nm in all fields of science (Amin et al. 2014). The materials at the nanoscale have distinctive structural characteristics, such as large porosity, high specific surface area, catalytic potential, and great pollutant binding capacities. In addition, nanomaterials could be modified easily by using organic or inorganic moiety, which makes them more reactive for specific pollutants (Qu et al. 2013; Bhati and Rai 2017).

Nanomaterials are classified based on their composition into three groups:

(a) **Organic nanomaterials**

Organic nano-sized carbon materials include graphene, fullerenes, carbon nanofibers, nanodiamonds, and carbon nanotubes (CNTs) [single-walled CNT (SWCNT) and multiwalled CNT (MWCNT)]

(b) **Inorganics nanomaterials**

Inorganics nanomaterials comprise metals (i.e., Al, Zn, and Fe) and oxide-based nanomaterials (i.e., Al_2O_3, ZnO, and Fe_2O_3). Noble metallic nanoparticles (AuNPs, AgNPs, and PtNPs) and nanomaterials metalloid (CdSe, ZnS, and ZnO).

(c) **Hybrid nanomaterials**

Different combinations are between organic nanomaterials and inorganic nanomaterials (Yuan and Muller 2010; Sebaa et al. 2013).

3.1 Carbon-Based Nanomaterials

Carbon-based nanomaterials (CBNs) are comprised of carbon atoms (Adeleye et al. 2016), and have unique characteristics that make them beneficial to remediation and purification of contaminated water (Thines et al. 2017; Ali et al. 2019). The most common CBNs include carbon nanotubes (CNTs), graphene, carbon nanofibers, fullerene, and carbon-based nanocomposites (Adeleye et al. 2016; Aguilar-Pérez et al. 2020).

3.1.1 Carbon Nanotubes

CNTs are tubes made of carbon with nanoscale diameters and commonly used as outstanding nanoadsorbent for toxic contaminants (Brar et al. 2010; Pyrzynska 2010; Herrero Latorre et al. 2012) owing to their unique sorption properties and layered geometric structure (Sui et al. 2012; Sweetman et al. 2012; Tan et al. 2012). CNTs are classified into: WCNTs and MWCNTs based on layers number in the structure. SWCNT contains a sole cylindrical graphene layer with a diameter of 0.4–2 nm, whereas MWCNTs consist of multilayer graphene sheets with 2–100 nm outer diameter and 1–3 nm inner diameter (Fig. 5). The CNTs are efficient sorbents capable of removing various pollutants from environment (Ma et al. 2011; Ren et al. 2011; Jin-Gang et al. 2014). Dehghani and his co-workers (2019) have used MWCNTs for OPPs (malathion and diazinon) removal from contaminated water. They reported effective removal of malathion in 30 min at pH 7 (Dehghani et al. 2017) and 100% removal of diazinon in 15 min from contaminated water (Dehghani et al. 2019).

CNTs are hydrophobic and are tended to agglomerate which lessen its capacity to retain pollutants (Jung et al. 2015; Ahmed et al. 2015). To overcome such drawback, supporter materials are used. Firozjaee et al. (2017) evaluated chitosan/CNT (CHN–CNT) as inexpensive sorbent for diazinon removal from aqueous solutions. A protected cross-linking method was used to incorporate CHN–CNT with 2.5% of MWCNT (Fig. 5). Results showed that CHN–CNT at a low concentration (0.5 g/L), exposure time (60 min), and pH (5.5) successfully removed >82.5% of the diazinon.

Metal–organic frameworks are hybrid materials which comprise metal clusters and multifunctional organic linkers. Liu et al. (2018) used magnetic MWCNTs @

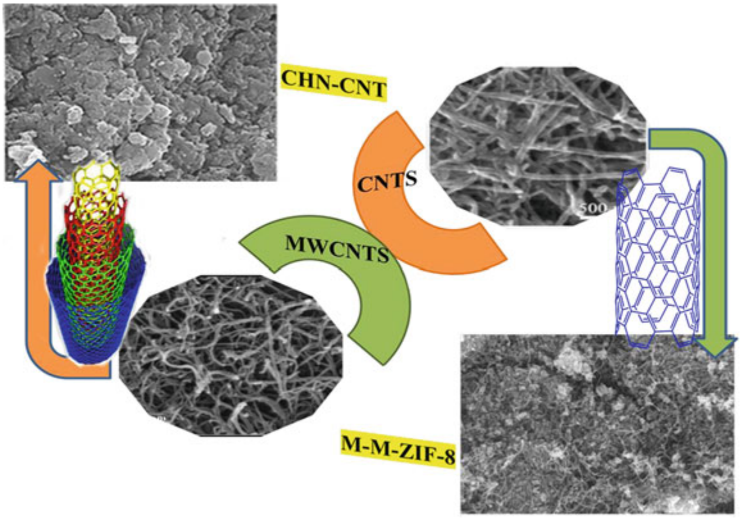


Fig. 5 Scanning Electron microscopy images of CNTS, MWCNTS and Chitosan/Carbon Nanotube (CHN-CNT) and (M-M-ZIF-8) organic framework ZIF-8/Magnetic multi-walled carbon nanotubes

organic framework ZIF-8 (M-M-ZIF-8) for OPP removal from contaminated water. The results showed the high capability of the hybrid sorbent (M-M-ZIF-8) for removal of OPPs (Table 2).

3.1.2 Graphene

Graphene is one of the most efficient nanomaterial to draw the attention of researchers. It is a hexagonal crystalline structure build up from two-dimensional layer of carbon atoms. The graphene-specific surface area is generally very high (2630 m^2/ g) which makes it a very promising sorbent for remediation of contaminated water. However, neighboring sheets of graphene in water tend to agglomerate owing to van der Waals interaction between graphene sheets. Since agglomeration negatively affected graphene surface area and pollutants adsorption, appropriate alteration of graphene is necessary to apprehend such unfavorable conditions (Zhao et al. 2012; Perreault et al. 2015). Graphene-based nanocomposites could be considered promising materials for OPP removal from the polluted environment (Fig. 6) (Aragay et al. 2012). Graphene family are repeatedly involved in treatment of wastewater (Pumera 2010; Wang et al. 2013; Qiu et al. 2018). Because graphene oxides (GO) are hydrophobic and contain hydroxyl, carboxyl, epoxide and carbonyl functional groups, they are considered excellent nanomaterials in retaining different pollutants in wastewater (Perreault et al. 2015). Maliyekka et al. (2013) and Yadav et al.(2019) reported distinctive characteristics of GO for chlorpyrifos and malathion adsorption from water with high maximum retention capacities of ~1200 and

Table 2 Maximum organophosphorus pesticides adsorption capacities of carbon-based nanomaterials

Adsorbent	Organophosphorus pesticides (OPP)	Adsorption capacity (mg g^{-1})	Reference
Chitosan/carbon nanotube (CHN–CNT)	Diazinon	222.86	Firozjaee et al. (2017)
ZIF-8/M MWC nanotubes (M-M-ZIF-8)	Triazophos	3.12	Liu et al. (2018)
	Diazinon	2.59	
	Phosalone	3.80	
	Profenofos	3.89	
	Methidathion	2.34	
	Ethoprophos	2.18	
	Sulfotep	2.84	
	Isazofos	3	
Reduced graphene oxide (RGO)	Chlorpyrifos	1200	Maliyekkal et al. (2013)
	Malathion	800	
Graphene oxide (GO)	Malathion	1666.666	Yadav et al. (2019)
	Chlorpyrifos	98.039	
Graphene coated silica (GCS)	Malathion	4.878	Liu et al. (2013)
Activated carbonized cellulose–graphene oxide composite (ACCE/G)	Chlorpyrifos	152.5	Suo et al. (2018)
Organo-zeolite (OZ)	Diazinon	1.35	Lemic et al. (2006)
HTAB–zeolite	Fenitrothion	1.66×10^{-6} mol/g	Lule and Atalay (2014)
DTAB–zeolite	Fenitrothion	1.67×10^{-6} mol/g	Lule and Atalay (2014)
Sodalite zeolite treated with dilute H_2SO_4 solutions (ATZ)	Diazinon	15.43	Esfandian et al. (2016)
Modified zeolite by Cu_2O nanoparticles (MZ)	Diazinon	61.73	Esfandian et al. (2016)
Dual metallic Zeolitic imidazolate frameworks (ZIF-2M)	Chlorpyrifos	98	Samadi-Maybodi and Rahmati (2020)
Zeolite imidazole frameworks ZIF-67 ZIF-8	Prothiofos	366.7 261.1	Abdelhameed et al. (2019)

800 mg g^{-1}, respectively (Table 2). OPP adsorption by graphene-based materials is reliant on adsorbent and adsorbate characteristics. Lazarević-Pašti et al.(2018) stated that the high oxidized graphene surface is not capable of adsorbing aromatic chlorpyrifos molecules, whereas the intermediate oxidized graphene surface is capable of adsorbing both aliphatic and aromatic pesticides.

The innovated graphene-coated silica (GCS) has proven to be efficient in removing 95% of nine OPPs from aqueous solutions (Liu et al. 2013). Suo et al.(2018)

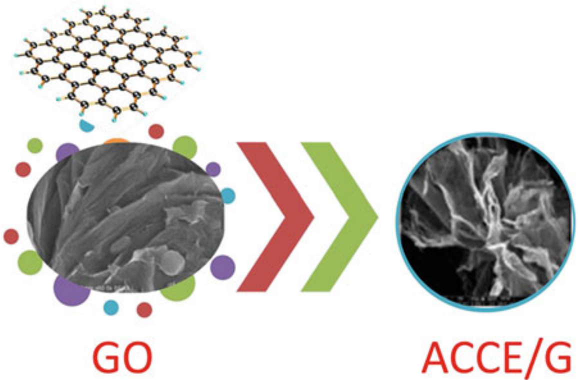


Fig. 6 Scanning Electron microscopy images of graphene oxide (GO) and activated carbon originated from cellulose/graphene oxide composites (ACCE/G)

produced graphene oxide/cellulose composites (ACCE/G) by using corn straw and tested it for the removal of several organophosphorus pesticides. The results clearly indicate the excellent adsorption capacity of ACCE/G toward the OPPs tested. However, the reported maximum adsorption capacity (MAC) of ACCE/G for chlorpyrifos was 152.5 mg/g which is much lower than that of RGO for chlorpyrifos (Table 2).

3.1.3 Polymeric Materials (Dendrimers)

Dendrimers are nano-sized, well-defined spherical, radically symmetric molecules which consist of a core, branches, and terminal functional groups to promote the action of distinct properties within the molecule (Fig. 7) (Tomalia 2010). The dendrimer interior branches could possibly be hydrophobic, whereas the terminal functional groups could possibly be hydrophilic, to permit hydrophobic molecules transportation through hydrophilic solutions.

The paramount privileges of polymeric materials are that they demand lower energy, and hence, lower regeneration costs (Srivastava et al. 2009). Durán-Lara et al. (2015) synthesized the nontoxic and lysine surface-modified polyester dendrimers [(2,2-bis(hydroxymethyl) propionic acid-bis-MPA]. The lysine dendrimers were evaluated for their capacity to remove dichlorvos (DCV) from contaminated water and their ability to efficiently capture the pesticide dichlorvos was demonstrated.

3.2 Zeolites

Zeolites are naturally micropore aluminosilicate minerals characterized by their high surface-to-volume ratio (Clariant Company 2013). Low-silica zeolites (Si/Al ratio < 2) acquire high cation exchange capacity (CEC), and it is widely used in

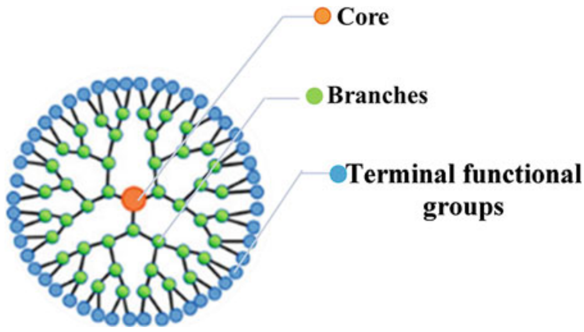


Fig. 7 The dendrimers structure

agriculture, industry, and water remediation particularly toxic metals and pesticides removal (Huong et al. 2016; Wen et al. 2016, Jiang et al. 2018). Ouznadji et al. (2014) have efficiently used zeolite (bentonite) for diazinon removal from aqueous media.

Yekta and Sadeghi (2018) synthesized and utilized zeolite AgX/CdO NPs composite catalyst for removal of fenitrothion from aqueous solution. Lule and Atalay (2014) modified natural zeolite with cationic surfactants to investigate its efficacy in removing fenitrothion from wastewater. The obtained results indicate the effective use of organo-zeolites in removal of fenitrothion. Esfandian et al. (2016) employed Si and Al (perlite) cheap sources for synthesis of sodalite zeolite using hydrothermal technique. The nano-sized of Cu_2O (4.5 wt.%). was loaded on the zeolite and the nanocomposite was used for removal of diazinon in fixed bed column (Fig. 7). Samadi-Maybodi and Rahmati (2020) have used Co and Zn metals to synthesize bimetallic zeolitic imidazolate frameworks (ZIF-2M) and employed it for chlorpyrifos removal. They reported that adding the second metal has improved crystal structure, porosity, specific area, and magnetic property of ZIFs and increased ZIF-2M removal efficiency to 97%. In a related study, Abdel Hameed et al. (2019) conducted an investigation on the efficiency of ZIF-2M for removal of prothiofos. The results have shown that MAC of ZIF-2M for prothiofos was 261.1 mg g^{-1} (Table 3).

3.3 Zero-Valent Iron Nanocatalysts

Nanosized zero-valent iron (nZVI) is characterized by intense reducing capability, large surface area, and ecofriendly (Zhang et al. 2019; Shao et al. 2020). Such properties have resulted to widespread application of nZVI for removal of dyes (Lin et al. 2008; Chen et al. 2011), and heavy metals (Rangsivek and Jekel 2005; Liu et al. 2010) and pesticides (Zhang et al. 2011; Singhal et al. 2012). However, the magnetic power of ZVI nanoparticles may cause agglomeration of these particles and limits its reactivity (Diao et al. 2016). In addition, nZVI can be easily oxidized with exposure

Table 3 Maximum organophosphorus pesticides adsorption capacities of zeolites

Adsorbent	Organophosphorus pesticides (OPP)	Adsorption capacity (mg g^{-1})	Reference
Organo-zeolite (OZ)	Diazinon	1.35	Lemic et al. (2006)
HTAB–zeolite	Fenitrothion	1.66×10^{-6} mol/g	Lule and Atalay (2014)
DTAB–zeolite	Fenitrothion	1.67×10^{-6} mol/g	Lule and Atalay (2014)
Sodalite zeolite treated with dilute H_2SO_4 solutions (ATZ)	Diazinon	15.43	Esfandian et al. (2016)
Modified zeolite by Cu_2O nanoparticles (MZ)	Diazinon	61.73	Esfandian et al. (2016)
Dual metallic Zeolitic imidazolate frameworks (ZIF-2M)	Chlorpyrifos	98	Samadi-Maybodi and Rahmati (2020)
Zeolite imidazole frameworks ZIF-67 ZIF-8	Prothiofos	366.7 261.1	Abdelhameed et al. (2019)

Table 4 Maximum organophosphorus pesticides adsorption capacities of nanoscale zero-valent iron (nZVI)

Adsorbent	Organophosphorus pesticides (OPP)	Adsorption capacity (mg g^{-1})	Reference
Chitosan/zero-valent iron nanoparticle composite (CS/nZVI)	Diazinon	64.93	Farhadi et al. (2021)
Fe/Ni bimetallic nanoparticles	Profenofos	0.202	Mansouriieh et al. (2016)
Silver Modified Zero-Valent Iron Nanoparticles (ZVINPs)	Temephos	12.65	Shiralipour et al. (2015)

to air which in turn limits nZVI reactivity (Ponder et al. 2000). In order to eliminate these problems, bimetallic Fe/Ni nanoparticles and supporting materials such as graphene (Xing et al. 2016), bentonite (Shi et al. 2011), and chitosan (Liu et al. 2010) have been practiced.

Mansouriieh et al. (2019) successfully used the bimetallic catalyst (Fe/Ni) for an OPP (profenofos) degradation and reported 94.51% removal.. Mehrotra et al. (2017) reported the efficient use of nZVI and Fe/Ni bimetallic nanoparticles for removal of dichlorvos in aqueous medium. Shiralipour et al. (2015) have used silver-modified nZVI for 99% efficient removal of temephos from aqueous solutions. The time needed for the complete temephos removal was less than 10 min. Farhadi et al. 2021 synthesized chitosan–nZVI (CS–nZVI) nanocomposite and used it for OPP (diazinon) removal from contaminated water. The achieved optimum conditions for successful removal of diazinon were 20 min contact time, pH 4.6, 0.05 g CS/nZVI dosage, and 100 mg L^{-1} initial diazinon concentration (Table 4).

3.4 Chitosan-Based Nanomaterials

Chitosan is the second largest biomaterial commonly used and distributed after cellulose (Mincea et al. 2012). It is generally produced from exoskeleton of crustaceans (i.e., shrimps, lobsters, and crabs). The crustaceans shells are removed, ground, and then processed further for chitosan production (Fig. 8). Chitosan can also be found naturally in some fungi and yeast (Illum et al. 2001). The structure of chitosan is quite similar to cellulose, in addition to hydroxyl groups, acetylamine or free amino groups (Hwang and Shin 2000). Recently, chitosan has attracted attentions because of its high adsorption capability for dyes (Uzun and Guzel 2004) (Table 5) and metal ions (Uzuna and Guzel 2000) owing to its enormous contents of hydroxyl and amino groups and its unique features, such as abundance, hydrophilicity, biocompatibility, biodegradability, and antibacterial property (Kumar 2000).

Abdeen and Mohammad (2014) used chitosan (CH) derived from biopolymer waste of marine industry for OPP (ethoprophos) removal from water. The results revealed that the highest removal percentage (89.23%) of ethoprophos was archived

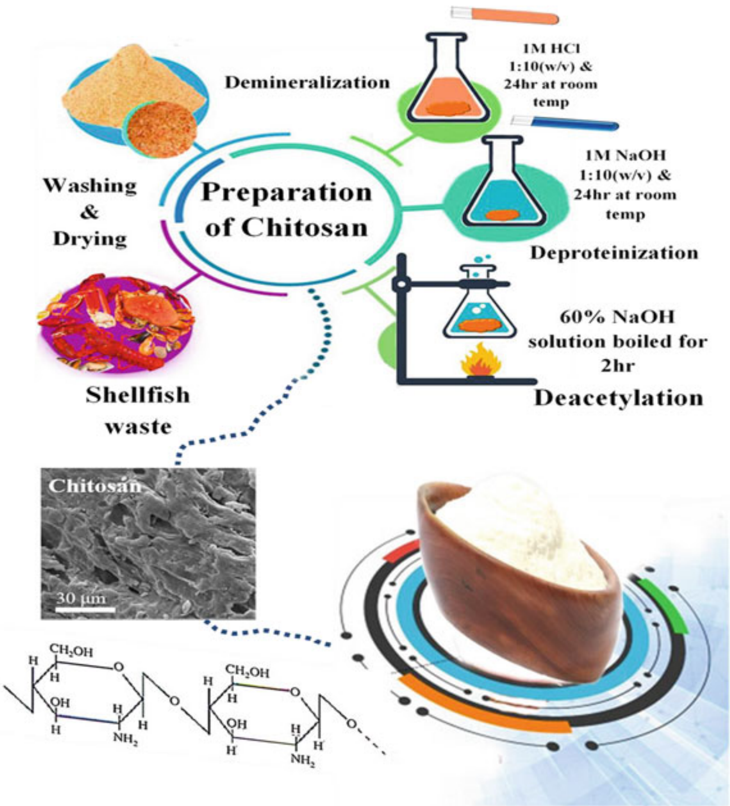


Fig. 8 Chitosan production

Table 5 Maximum organophosphorus pesticides adsorption capacities of chitosan-based nanomaterials

Adsorbent	Organophosphorus pesticides (OPP)	Adsorption capacity (mg g^{-1})	Reference
Chitosan (CH)	Ethoprophos	85.47	Abdeen and Mohammad (2014)
Mixed hemi micelle SDS-coated magnetic chitosan nanoparticles (MHMS–MCNPs)	Diazinon	16.58	Bandforuzi and Hadjmohammadi (2019)
	Phosalone	15.53	
	Chlorpyrifos	13.48	
Copper chitosan nanocomposite (CuCH)	Malathion	322.6	Jaiswal et al. (2012)
Gold nanoparticle chitosan composite hydrogel beads (GNP–gel beads)	Methyl parathion	58.6 μmol g^{-1}	Dwivedi et al. (2014)

by using the adsorbent dose of 0.1 g/100 mL. Because chitosan (CS) has unique characteristics such as nontoxicity, abundance, and biodegradability, it is used with other nanomaterials to construct nanocomposites. In addition, CS can form a chelate due to hydroxyl (–OH) and amino (–NH_2) active groups on its surface (Farhadi et al. 2021). Jaiswal et al. (2012) produced and evaluated a novel copper chitosan nanocomposite for the malathion elimination. They indicated that the maximum adsorption capacity of the nanocomposite was quite high (322.6 mg g^{-1}).

Magnetic chitosan nanoparticles have been reported as an effective sorbent capable of removing more than 96% of diazinon, phosalone, and chlorpyrifos from contaminated water (Bandforuzi and Hadjmohammadi 2019). Badawy et al. (2018) have prepared novel chitosan–siloxane functionalized magnetic nanoparticles using Fe_3O_4 functionalized-siloxane derivatives and coated with chitosan through a crosslinking mechanism. The produced nanoparticles were used successfully as effective sorbent for extraction of diazinon and fenamiphos from water (Table 5).

3.5 *Silica-Based Nanoparticles*

Silica NPs (SNPs) are amorphous materials which possess a high content of silanol groups (Si–OH) or siloxane groups (Si–O–Si) (Sharma et al. 2015). Silanol groups provide a highly reactive surface that could be beneficial to the adsorption process due to the effective sorption capacity of their functional groups for target contaminants (Hossaini et al. 2014; Soltani et al. 2015). Silica nanoparticles are prepared from alkoxides silicon alcohol solution in association with ammonia catalyst which prompts variable sizes of SNPs ranging from 50 to 1000 nm. This method could be manipulated for several applications of SNPs (Fig. 9).

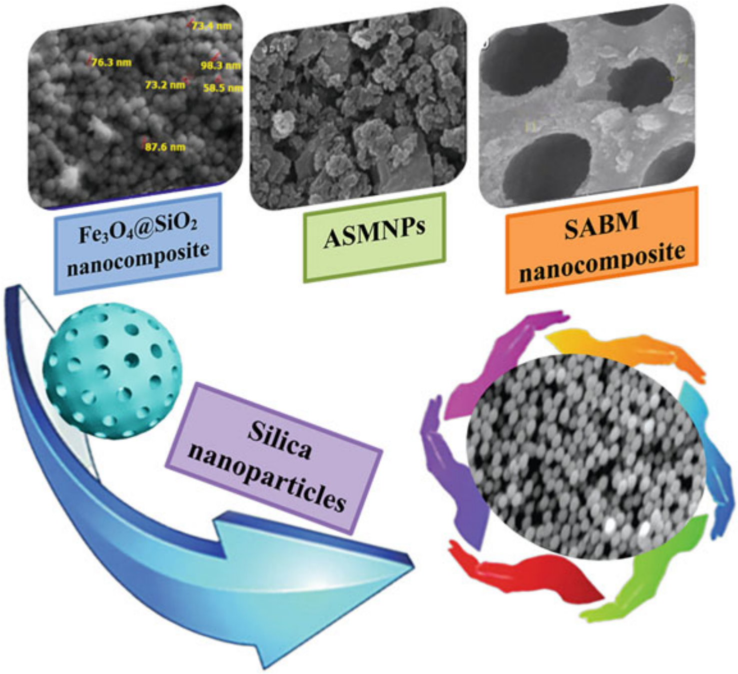


Fig. 9 Scanning Electron microscopy images of silica nanoparticles, Sodium Alginate/Biosilicate/Magnetite Nanocomposite (SABM) and silica-coated magnetic nanoparticles through an amine functionality (ASMNPs)

Moliner-Martinez et al. (2014) have used silica supported Fe_3O_4 nanoparticles as a sorbent for OPPs removal from water samples. The achieved results were satisfactory and the efficiencies of chlorfenvinphos and chlorpyrifos sorbents' removal were 60 and 84%, respectively. Such perspective offers a promising technique for water treatment using nanocomposites. Similarly, Shamsizadeh et al. (2020) synthesized $Fe_3O_4@SiO_2$ nanocomposite with 96% removal efficiency of diazinon from aqueous solutions (Table 6).

Hosseini et al. (2019) evaluated the efficiency of sodium alginate/biosilicate/magnetite (SABM) nanocomposite in malathion removal from water environments. The highest removal efficiency of SABM (94.82%) for malathion was obtained at optimum pH 7, 120 min contact time, 4 g/L adsorbent dosage, and 318°K.temperature. Silica-coated magnetic nanoparticles were used for preparation of a recoverable adsorbent using amine functionality for efficient diazinon removal from contaminated water. The optimum diazinon removal achieved was of 84% within 30 min (Table 6) (Naeimi Bagheini et al. 2018).

Table 6 Maximum organophosphorus pesticides adsorption capacities of silica-based nanoparticles

Adsorbent	Organophosphorus pesticides (OPP)	Adsorption capacity (mg g^{-1})	Reference
Fe_3O_4@SiO_2 magnetic nanocomposites	Diazinon	10.90	Shamsizadeh et al. (2020)
Sodium Alginate/Biosilicate/Magnetite Nanocomposite (SABM nanocomposite)	Malathion	36.86	Hosseini et al. (2019)
Fe_3O_4@SiO_2@GO-PEA	Chlorpyrifos	Mix were 32.6	Wanjeri et al. (2018)
	Parathion		
	Malathion		
Silica-coated magnetic nanoparticles through an amine functionality (ASMNPs)	Diazinon	112.36	Naeimi Bagheini et al. (2018)

3.6 Nanostructured ZnO Semiconductor Films

The nanosized zinc oxide (ZnO), with one dimension less than 100 nm, mainly consisted of single mineral (ZnO). It may incorporated with other material to modify the chemistry and function of the nanoparticles for effective use of different technologies. Several nanoparticles can be fabricated from ZnO using simple and cheap techniques, such as the sol–gel method (Li et al. 2014), spray pyrolysis (Tarwal et al. 2014), and hydrothermal synthesis (Tshabalala et al. 2017). Heterojunction with other metals or metal oxides was also introduced to enhance the sensing ability of ZnO (Zhang et al. 2015; Xu and Ho 2017). The low cost, high photosensitivity, stability, and ability of nanoscale zinc oxide to degrade different pollutants received much attention lately.. For instance, Serrano-Lázaro et al. (2020) proposed the use of nanostructured ZnO photocatalyst films to degrade Temephos.

Aghaei et al. (2020) synthesized the coupled metal ZnO–CuO using the sonoco-precipitation method and evaluated it for photocatalytic degradation of parathion. The coupled metal fully degraded (100%) parathion after 60 min sono-photoirradiation under optimal experimental conditions. In addition, Sharma et al. (2016) studied the photocatalytic degradation of parathion (PA) and methyl parathion (MP) using UV–ZnO nanocrystal. Degradation of 93 ± 2.5% of MP and PA was achieved which indicates the efficacy of photonano-catalyst for the decomposition of OPPs.

3.7 Nanowater Treatment Residuals

Several industrial by-products showed excellent adsorption capacity and consequently used for removal of organophosphorus pesticides(OPPs) from polluted

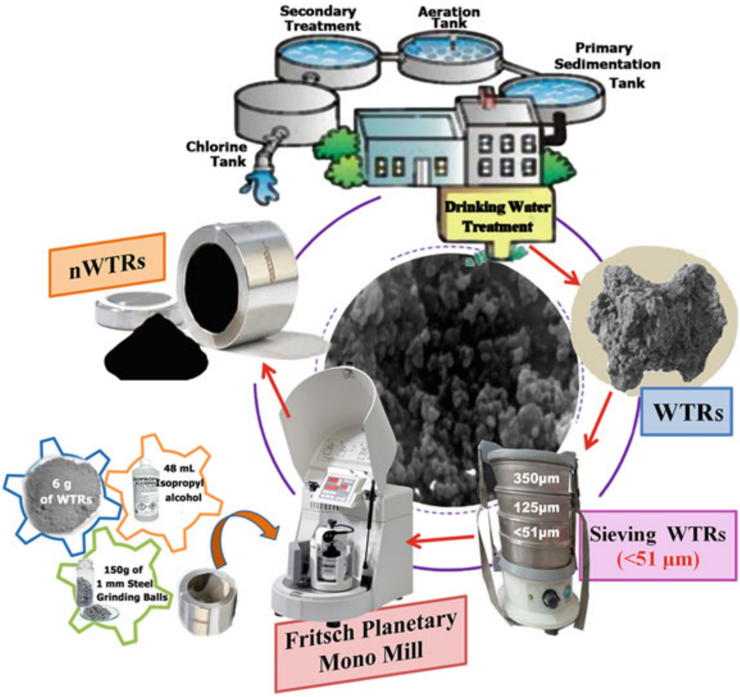


Fig. 10 Producing nanoparticles originated from water treatment residuals (nWTRs)

water. These by-products are readily available and can be obtained free of charge which favored its practical application and use as sorbents.

Water treatment residuals (WTRs), also called "alum sludge," are waste products of water industry, where undesirable contents of the raw water such as turbidity, organic chemicals, biological particles, and suspended solids are removed through coagulation using aluminum (Al) salts. WTRs have a large surface area (105 m^2 g^{-1}) and plenty of active sites which privileged its use in water remediation (Makris et al. 2004; Elkhatib et al. 2021). Various studies have indicated the capacity of WTRs for removal of organic and metal contaminants (Caporale et al. 2013; Elkhatib et al. 2013; Elkhatib and Moharem 2015; Moharem et al. 2019; Turner et al. 2019; Li et al. 2020). Zhao et al. (2013) indicated the ability of WTRs to remove chlorpyrifos from polluted water with a low maximum adsorption capacity for chlorpyrifos (1.2 mg/g). Therefore, attention lately has focused on beneficial reuse of WTRs nanoparticles for removal of OPPs (i.e., chlorpyrifos) from contaminated water.

Hamadeen et al. (2021a) have produced the nanosized WTRs (nWTRs) by the method of Elkhatib et al. (2015) and used nWTRs for chlorpyrifos (CPF) removal from polluted waste water (Fig. 10). The experimental results have shown fivefold increase in the MAC of nWTRs for CPF (50 mg g^{-1}) in comparison with sorption capacity of bulk WTRs.

3.8 *Nanosized* Moringa oleifera *Seeds Waste*

Biosorption is an emerging green technology that offers cheap sorbents of biological origin (Medhi et al. 2020). Several biomaterials could be employed as cost-effective biosorbents, such as waste products from food industry. The by-product residue (seed cake) of oil extraction process from *Moringa oleifera* seeds has been reported to have high affinity for pesticides (Pavankumar et al. 2014; Ramachandran et al. 2015). Today, one of the key focus research areas of waste water remediation is substituting the high priced commercial nanomaterials with inexpensive effective nanosized biosorbents derived from the abundant lignocellulosic by-product wastes. Recently, Hamadeen et al. (2021b) have used the abundant Moringa seed waste (MSW) to produce ecofriendly efficient nanosorbent for remediation of chlorpyrifos (CPF)-contaminated wastewater. After oil extraction from *Moringa oleifera*, the by-product seeds waste was subjected to dryness for 1 h at 60 °C and ground mechanically following the technique of Elkhatib et al. (2015) to reduce the particles size of MSW to nanoscale level (Fig. 11). The nanosized MSW (nMSW) was evaluated for its efficacy for elimination of CPF in polluted wastewater. The experimental results have shown that the nMSW was 275% more efficient than the bulk MSW in CPF removal from wastewater (Hamadeen et al. 2021b). Moreover, the kinetics, thermodynamics, and Fourier transformed infrared spectroscopy studies exposed the involvement of the associative mechanism, electrostatic attraction, H bonding, π interactions, and hydrophobicity in the CPF sorption process by nMSW sorbent (Fig. 12). In brief, the high decontamination potential of nMSW

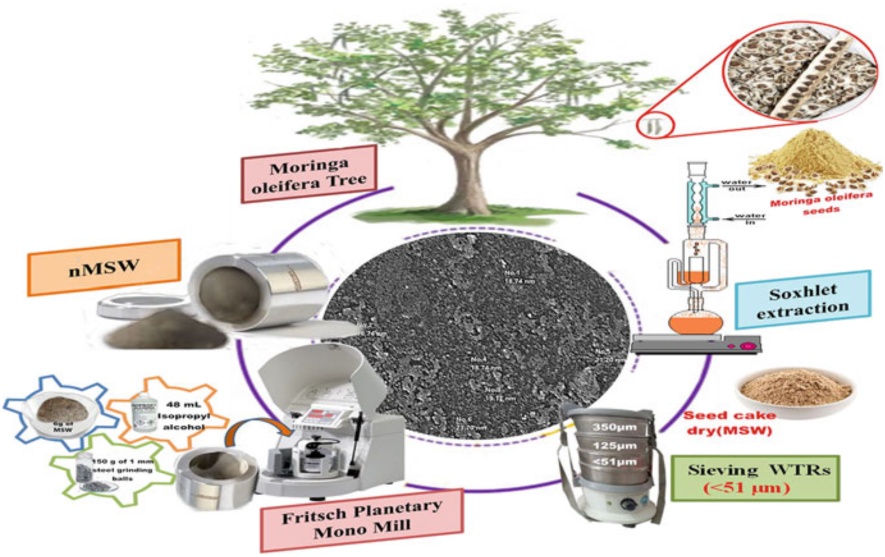


Fig. 11 Namostructured–biosorbent originated from seeds waste of Moringa Oleiferea (nMSW)

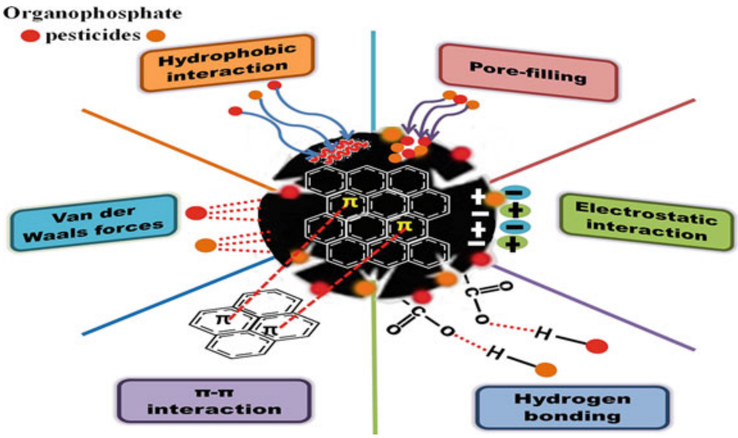


Fig. 12 Different interactions between organophosphates pesticides and nanomaterials

recommends its use as an efficient, green, and cost-effective option for wastewater treatment.

4 Parameters Affecting OPPs Adsorption Process

Adsorption is a mass transfer process, where the soluble species from liquid gets deposited on/attached to the surface of solid because of physical or chemical interaction (Babel and Kurniawan 2003). Diverse range of nanomaterials have been used to explore their capabilities in removing organophosphate pesticides (OPPs) from contaminated water through the adsorption process. Nevertheless, for efficient OPP adsorption by different materials, optimization of the operation conditions like solution pH, temperature, and sorbent dosage is necessary. In the following, the factors controlling OPP's sorption by different nanomaterials are interpreted.

4.1 Effect of pH

Solution pH is a critical parameter greatly affecting OPPs retained on the adsorbents' surface, because surface charge of the adsorbents and OPPs may change with changes in pH. Therefore, the effect of solution pH should be evaluated to identify the optimal pH value required for the highest adsorption capacity of the sorbent. Bahrami et al. (2018) conveyed that the electrostatic interaction between OPP molecules and adsorbents surface is greatly affected by initial pH. Mansouriieh et al. (2019) demonstrated that profenofos (PFF) adsorption decreased as the pH decreased due to protonation of the PFF molecules and increasing the repulsion forces between PFF the positively charged molecules and the similar charges of the sorbent surface. Opposite trend was observed by Hamadeen et al. (2021a,b) who reported lower CPF removal percentage at high pH (alkaline) values because of the deprotonation of OH group on the sorbent surface which limits formation of hydrogen bond between the sorbent and OPP.

4.2 Effect of Contact Time

Contact time is a critical criterion that affects the maximum sorption capacity of the sorbents. The minimum contact time required for the sorbate to interact with the sorbents is critical and depends on surface characteristics of the sorbents and the sorbates (OPPs). At or near equilibrium, the adsorption process slows down and becomes constant which indicates that the adsorption process is complete and all the vacant sites on the sorbent surface are filled. Thus, the contact time between particular sorbate concentration and sorbent to reach equilibrium is a governing factor in the adsorption technique and should be optimized (Srivastava et al. 2015; Sajid et al. 2018).

4.3 Effect of Adsorbent Dose

Efficacy of sorbents for removal of OPPs molecules relies on active sites number on sorbent surface, i.e., adsorbent dose. The quantity of adsorbate by unit mass of adsorbent generally increases with increasing adsorbent concentration (active adsorption sites). However, the extent of adsorption may decrease with increasing sorbent concentration due to the competition and interaction with adsorbate molecules for adsorbent active sites (Esposito et al. 2001; Das and Das 2013; Xie et al. 2015). Hamadeen et al. (2021b) investigated the optimum dose of nanoparticle derived from moringa seed waste for chlorpyrifos (CPF). They found that removal of CPF increased with decreeing adsorbent dose. On the contrary, Kütahyali et al. (2010) reported that the percentage removal of the contaminant increased with increasing the Pinus brutia leaf dose from 0.05 to 0.45 g, Thus, optimization of adsorbent dose is crucial for efficient OPPs' removal.

4.4 Effect of Temperature

The mobility of the contaminants at solid/liquid interface is greatly affected by the temperature (Iftekhar et al. 2017). Ramasamy et al. (2017a, b) examined effect of increasing the temperature from 25 to 60 °C on the adsorption process of some contaminates. The results affirmed that adsorption of the contaminants by modified silica gel and the removal efficiency of the contaminants were significantly increased with temperature rise. The increase in removal efficiency of the studied contaminants with increased temperature could be due to new sites formation and pores enlargement (Hashemian et al. 2013). However, opposite results were reported for the removal of chlorpyrifos (CPF) by nanoparticles of water treatment residuals, carbon and graphene oxides. Nodeh et al. (2019) and Hamadeen et al.(2021a,b) reported that the removal efficiency of CPF by the sorbents studied was unfavorable and low temperature reinforces CPF adsorption onto the studied sorbents. Therefore, influence of temperature should be optimized to determine the impact of temperature on the adsorption process.

5 Sorption Mechanism

The sorption mechanisms involved in OPP sorption by the nanomaterials include electrostatic interaction, Van der Waals forces, pore-filling, hydrogen bonding, organo-metal complexes, hydrophobic interaction, and π–π interaction that describe the intermolecular bonding between OPPs and nanomaterials. The driving force of one over other mechanisms relies on the nature, structure, chemical as well as physical characteristics of OPPs and the nanosorbents.

Hydrophobic interactions are the tendencies of two nonpolar substances (hydrophobes) to agglomerate (Meyer et al. 2006). Such interactions are most common between OPPS and carbon nanotubes. Hamadeen et al. (2021b) observed large partition of CPF into the organic fractions of the sorbent due to the moderate hydrophobicity level of CPF.

Electrostatic interactions are the attraction or repulsion between oppositely charged molecules or identically charged molecules, respectively (Tourinho et al. 2019). In general, high solution pH is linked to strong electrostatic due to the influence of pH on the surface electric potential (zeta potential) and the high sorption capacity (Padilla-Ortega et al. 2014; Xu et al. 2018). When the pH of the aqueous media is higher than that of zero point of charge (pHpzc) of the sorbent, its surfaces acquire negative charges and its capability to attract positive charge ions (Liu et al., 2018). Hamadeen et al. (2021b) reported electrostatic interactions between S, O, N, and Cl anions of chlorpyrifos and C–O, NH_2 atoms of nanoparticles derived from moringa seeds waste (Fig. 12).

The pore-filling mechanism is referred to enter the molecules of the contaminants and trapped in the pores of the nanosorbents.

Hydrogen bonds exist between a pair of atoms in different molecules, where one atom of the pair (the donor, i.e., F, N, and O) effectively shares its hydrogen with the acceptor atom forming a bond (–FH, –NH, or –OH). Such an interaction supports the removal of organic pollutants capable of forming hydrogen bond such as phenol in OPPs. Olivella et al. (2015) reported the capability of O atoms of chlorpyrifos to form H-bonds through the OH of the raw cork lignin (Fig. 12).

Van der Waals forces are weak intermolecular forces between uncharged atoms or molecules of all organic liquids and solids. These forces are easily vanished with increasing the distance between the interacting molecules to more than 0.6 nm. The adsorbed organic pollutants on adsorbent surface by Van der Waal's forces are easy to remove. Van der Waals forces are generally improved by hydrogen bonding.

π–π interactions are a type of noncovalent interactions which act between aromatic molecules (Bakir et al. 2014; Tourinho et al. 2019) like adsorption of organic contaminants by carbon nanotubes.

6 Future Perspectives

Emerging organic contaminants have recently captured substantial recognition due to the urgent demand for its removal from the environment. Despite the critical discourse analysis and the substantial research in the adsorption process, it has been recognized as a primary selection due to the economic cost of the process. At present, nanotechnology is considered as one of the most attractive research areas in water remediation sector due to its unique characteristics and applications. It is paramount for the future studies in water treatment sector to bring into focus on the cost-effective green nanomaterials with greater efficiency and sustainability. Studies also need to be focalized on the nanobiosorbent application for OPP removal from contaminated water. Moreover, batch studies must be associated with column studies for more complete picture of adsorbate–adsorbent interactions. Developing cost effective nanomaterials capable of simultaneous removal of emerging and inorganic contaminants from real waste water is indispensable. It is also encouraging to search for economic green nanosorbents with greater selectivity and sustainability. In addition, translating research findings of potential low-cost nanosized green sorbents from lab scale to industrial scale is required in the years to come.

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Collateral Effects of Nanopollution on Human and Environmental Health

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1 Introduction

Currently, most nanotechnology (NT) components grow and evolve with scarce laws or restrictions worldwide. This might harm employees in both indoor and outdoor environments. This sort of material has recently received a lot of interest owing to our increasing ability to create nanoparticles (NPs). NPs are employed in many fields, including electronics, medicine, cosmetics, agriculture, and environmental activities. Due to the enormous promise of this technology, international expenditures in nanotechnology are increasing. Therefore, the industry is now very interested in NTs due to its novel uses in diverse industrial, agricultural, or environmental sectors. In rare new situations, scientists or decision-makers must profoundly and quickly examine their influence on the environment and living beings (Perez-Hernandez et al. 2021).

The absorption rate of NPs by mammalian or vegetal cell membranes depends on their size. For calculating absorption rates, the NP size and their dispersion, aggregation, and sedimentation in cells are critical. Besides, NPs are absorbed by specific cells through endocytosis or phagocytosis. Small particles, such as NPs, are stored in

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the mitochondria of cells and may induce harmful responses (Begum and Jayawardana 2021). NP's toxicity is linked to size, surface area, and propensity to create reactive oxygen species. In multicellular species, NPs produce inflammation and fibrosis, whereas, in unicellular creatures, they cause cytotoxicity and antioxidation. Nanosized particles induce respiratory and cardiovascular problems in people. Polycyclic aromatic hydrocarbons (PAHs) and extremely fine soot may penetrate deep into the lungs and induce harmful consequences, while NP-associated diseases may cause early mortality in the gas, coal, asphalt, and industrial sectors. Models of various sorts of organisms, ranging from microorganism to complex animal species, are used to assess the potential toxicity of nanomaterials (NMs) in order to determine their safety (Martinez et al. 2021; Valle-García et al. 2021).

Several studies have reported the negative environmental impact of NMs through the absorption and distribution inside the organisms (Khan et al. 2021). Therefore, mechanisms or processes regarding NMs toxicity have been well-studied during the last years, giving evidence about the oxidative stress triggered by reactive oxygen species (ROS) due to the presence of nanosized materials (Mo et al. 2021; Pinheiro et al. 2020; Wu et al. 2020). Besides, owing to the expanding usage of NMs in numerous sectors, all members of society are exposed to the toxicity of these nanoparticles. These tiny particles harm several organs, including the reproductive system. Therefore, NMs may also cause abortion in women, embryonic stunt growth, and harm men's reproductive systems and sperm morphology (Ajdary et al. 2021). Despite changes in nanoparticle composition, concentration, and delivery route, reproductive organs are still damaged in certain situations, according to Ajdary et al. (2021) and Souza et al. (2021).

Once in the environment, NPs' influence is determined by their potential to introduce, accumulate, and aggregate in organisms and cause damage or their capacity to harm or hazard the ecological equilibrium and resilience. Therefore, this chapter aims to discuss the collateral effects of nanosized products synthesized and released for human or environmental benefits.

2 Nanopollution

The concept of nanotechnology involved the manipulation of matter in nanoscale form, the nanomaterials (NMs) obtained by nanotechnology, had many applications in human life as energy conversion and storage, water cleanup, and purification, also for biomedical equipment and nonetheless important consumer products. This nanosize permits the NMs to have enhanced interaction with biological structures when present in the human daily products, afterward the NMs enter waste streams through the household's waste. Some of the consequences of the presence of NMs in wastes are the impacts on the environment, human health, and living organisms, this impact could be defined as nanopollution (Chaturvedi and Dave 2021).

Figure 1 shows the graphical flux of the nanoparticles (NPs) going through the environment when these NMs are present in the air, water, and soil, and remain

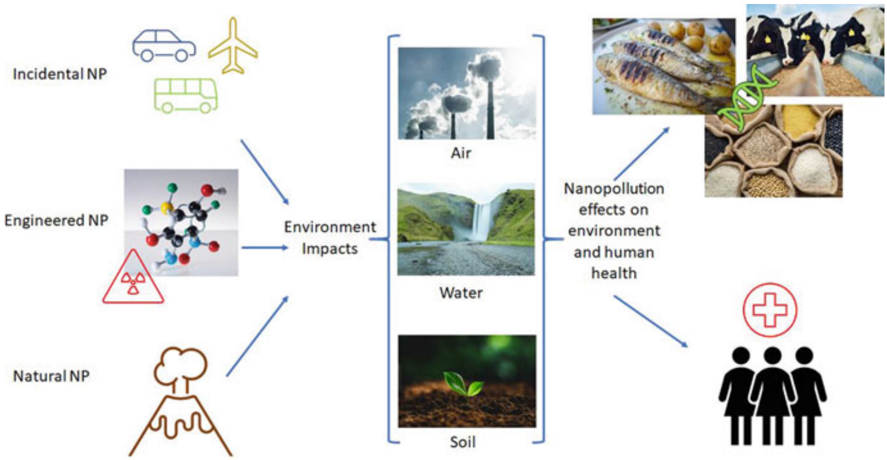

Fig. 1 Nanoparticles (NPs) flux to nanopollution in the environment and human health

present in the organisms, affecting not only human health, but also the plants and animals reproduction and viability.

The NMs that are produced naturally on the Earth are called Natural NMs or Natural NPs, which are normally formed through different biogeochemical processes as natural chemical weathering processes, volcanic eruptions, aeroplasma lightning, flash pyrolysis, metal, and metal oxides NMs formed by biotic or abiotic interactions. Other sources of NMs are de incidental ones, coming from anthropogenic activities, normally coming from automobile combustion, industrial waste, mining waste, and textile industries, among others. The engineered NMs (ENMs) are the ones engineered for different activities or applications as the energy sector, agrichemicals, and personal care products principally, some NMs can be grouped based on their morphology as quantum dots, nanorods, graphene, or fullerene, for its dimensions, and other ones by their composition as carbon or metal-based NM, but some NMs can be grouped in two groups as well (Malakar et al. 2021).

Many NPs are present in drinkable waters as $CaCO_3$ and $CaSO_4$, which are often laced to other elements as iron oxides, but this NM that is naturally occurring has poor quality and is not perfectly shaped or well-defined as the synthetic ones. NP generated by natural nanosizing is not common in the environment, but the incidental ones as the fine platinum particles are released from cars and its catalysts used for the combustion, such as abrasion from tires, affecting not only the environment but also human health eventually (Griffin et al. 2017).

NP can be as harmful as beneficial to the environment, and the effects could affect positively or negatively to microbes, plants, and humans. Somewhere else, TiO_2 NPs are beneficial for seed germination and also enhance the root–shoot length in Arabidopsis thaliana, cabbage, corn, lettuce, oat, and flax. In contrast to these benefits, the AgNPs are reported to be toxic to heterotrophic microorganisms as well as autotrophic plants (Shweta et al. 2018). As it seems in the agricultural field, there exists a close relationship between agriculture and NMs, meanwhile, NPs are used to expand treatment enhancing the proficiency, yields, and diminishing pesticide requirements, but these nanotechnologies have to be treated with care, and there exist unforeseen risks together with their positive potential. The nanotoxicity effects on humans and health increased due to that NMs enter the human body very easily, in different ways, mainly via respiratory, dermic, and gastrointestinal (Mukherjee et al. 2019).

NMs that have driven much attention for their properties is graphene oxide (GO), which has been utilized in different applications, such as in industry as in medicine, but there are not many reports about the effects of these NMs in the environment. Some studies, in bacteria and animals, were exposed to GO showing side effects, as intensifying the mechanisms of antioxidative defense from cells; in a consequence, the reactive oxygen species (ROS) were generated in them, and is indirectly responsible for protein and genetic material damage, disrupting the cell cycle. The long exposure is less studied in terms of GO effects in the environment, in a study using Acheta domesticus, an insect which is a polyphagous species from cricket was feed with a mixture of pellets containing protein, plant components, and GO NP solution (50 mg/mL). The obtained results indicated a significant decrease in reproduction capabilities, evidenced by the lower numbers of laid eggs and decreased success in hatching, also it was demonstrated the low cell viability in the next generation compared with their parental generation, inferring that GO has long-lasting effects in the organisms generations (Dziewięcka et al. 2018).

When NMs are released into water, they are potentially transformed due to their colloidal stabilities and aggregation, nonetheless, the type of aqueous media affects their composition, and several methods and procedures have studied the modification of NMs and aid in improving their solubility in water. Moreover, the use of NP-treated products, as clothing and detergents, is released into the environment, an example of this, are the use of AgNPs in socks, which are reported to leach out after three items of washing. Another example are the fullerenes C60 and C70, which were observed suspended in wastewater sediments, river water, soils, and atmospheric particulate matter (Saleh 2020).

The nanoscale zinc oxides (nZnO), are another NPs to consider as nanopollutant, these NMs are commonly used in UV screens and antimicrobials, nowadays has been studied its effects on coastal marine ecosystems, affecting negatively the growth, immunity, and reproduction of marine organisms. In aquatic ectotherms, its metabolism is susceptible to temperature and contaminants, especially to nanopollutants, like TiO_2 and Ag NPs, both are reported inhibitors of feeding activities, diminishing food absorption efficiency causing impaired digestion, and by consequence decreasing the growth of marine mussels as *M. edulis* and some clams. The effect study of nZnO in blue marine mussels showed that at high temperatures in summer additional with NP's presence, has a negative effect reducing the lipid content in tissues causing immobilization of carbohydrates, and a side effect, is that the organisms cannot cover the energy necessary for its biological functions (Wu et al. 2021).

In a study, using *Artemia* sp. naupli, which is a genus accepted as a model organism for measuring contaminants in aquatic environments, it was observed the effect of Ag NPs in the organism before mentioned, and in Artemia salina, both were treated under different conditions as different lights, salinities rates, temperatures, etc. It was observed that these microcrustaceans, that are non-selective feeder capable of ingesting NPs, presenting bioaccumulation in their tissues, and also it was reported that Ag ions can be accumulated and being toxic to the organisms and cannot remove easily from the sediments, inclusive it was suggested that the temperature and the concentration of NPs have a relationship with these NP accumulation (Asadi Dokht Lish et al. 2019).

The effects in organisms that live in water bodies by the ZnO have been studied in different processes like adsorption, aggregation, dissolution, and concentration. In these aquatic environments, the interaction between ZnO NPs with *Chlorella* sp. had collateral effects as deformed algal cell, the morphology of algae, decreasing viability and the membrane integrity is compromised, these effects happen due to the dissolution of ZnO into Zn_2^+ ions, and as consequence damage cell walls from the algae, reducing the cell growth and chlorophyll concentration in marine phytoplankton. Another effect that has been observed is that the NPs can sediment in the aquatic environments and form aggregates of NPs, and are forming part of the sediments, affecting the benthic organisms and filter feeders, generating NPs bioaccumulation and biomagnification in food chains, resulting in nanopollution (Sharan and Nara 2019).

An area that has fewer studies about their environmental effects are plastics, which have been the perfect choice for many applications due to their low cost, lightweight, durability, and versatility. Some examples of plastic polymers include polyamide (PA), polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). A considerable amount of these plastics are accumulated in the aquatic environment, and some of them are designed to be biodegradable, which in a lapse of time will be transformed into small pieces of plastics, that will affect the aquatic biota (Thiagarajan et al. 2021).

These plastics could be classified based on their size as nano plastics (<1 μm) and microplastics (<5 mm). The environmental impact of micro/nanoplastics (MNPs) is physical and chemical due to their ability to adsorb and accumulate co-contaminants. The MNPs have a vector effect due to the ability of metals and organic pollutants to adhere to MNPs and get transported to the animal gut and finally are considered the toxic effect on these organisms. The vector effect of MNP-mediated transport can be categorized into three types: environmental, organismal, and cellular. Somewhere else is reported that the MNPs increased their hydrophobicity when triclosan is adsorbed by the NPs, and the consequence of this effect is the precipitation in the water column and consequently reduces the bioavailability and direct toxic effects of triclosan to the marine microalgae, *Skeletonema costatum* (Thiagarajan et al. 2021).

NMs can be transferred to the soil from aqueous media or air, and some parameters are important for this transference and are depending on the type of NMs and their functionalities, the nature of the solid phase or soil, and its components. The transfer level of NMs depends on the partitioning of the solid phase and the aqueous phase, and this partitioning can occur in these mechanisms as mentioned: (i) adsorption, which depends on the hydrophobic properties of NMs and the nature of the solid phase to which it is adsorbed; (ii) formation of covalent, ionic, and coordination bonds; (iii) electrostatic interactions; and (iv) the aid of some NMs additives such stabilizers, natural organic carbon, or surfactants, used to assist de dispersion of NMs. The popular transfer path of NMs into wastewater is based on the homogeneity of NMs with the solid and water phases. One example is titania NPs, which are accumulated in sewage sludge during the wastewater treatment; afterward, these sludges are deployed to the soil in several different places (Saleh 2020).

The CoO NPs have been less studied, but some effects that are observed are similar to ZnO NPs, both had been found that generate toxicity not only in ionic form, also can be nanotoxic in particulate form, but the metal ions can also enter the cells through ion channels or by transporters present in the cell wall surface, and NPs enter via endocytosis or by ion channels at the same time. The CoO as phytocontaminant showed toxic effects on Allium cepa, which is a terrestrial plant, and in this study, it was observed massive aggregation around the root system of A. cepa, affecting the root morphology and the cellular network (Sharan and Nara 2019).

The CuO NPs had increased their production due to applications in the industry and afterward are released into the environment creating risks to plants as the *Hordeum sativum distichum*, which is an important example of food crop, obtaining as a result that CuO NPs affects the germination rate, root (decreasing 35% of the length), and shoot lengths (decreasing 10%), the maximal quantum yield of photosystem II, and transpiration rate. In addition, there were observed structural changes in the chloroplast, vacuoles, mitochondrial, and stomatal structure (Rajput et al. 2018).

Some NPs as CuO and ZnO, are utilized as nanopesticides and nanofertilizers, which are concerning the soil and agro-environment pollution, due to these applications, can be speculated that more than 95% of Cu used, eventually ends at the soil and aquatic environments in a concentration up to 500 μg kg^{-1}, in case of ZnO is estimated ~16 μg kg^{-1}. The NPs differ in their speed of transformations depending on their aggregative state, and nonetheless important are the soil characteristics like pH, organic matter, or water content, which will mediate the dissolution of NPs in soil, converting them to ions. The accumulation of NPs in plant tissues impacts human health due to the ingestion of these bioaccumulators (Rajput et al. 2020a, b).

MoS2 NMs are transformed when they are released into the environment, the behavior of these NPs depends on their characteristics as in the environmental conditions including light illumination, pH, oxygen, natural organic matters (NOMs), and ionic strength. The physicochemical transformation occurring in MoS_2 includes aggregation, adsorption, deposition, and dissolution. In the case of NOMs which is formed by humic acid (HA) and fulvic acid (FA) present in many environments as the aquatic ones, the main function of the NOMs is the regulation of environmental transformation and biological toxicities of NPs by changing the surfaces properties through non-covalent interactions. MoS_2 can be oxidized by oxygen or other oxidizing agents, leading to the release of soluble species. The residual MoS_2 materials in natural waters, soil, and sediments may directly harm living organisms. Moreover, these NMs can be accumulated and transformed into living forms and finally be consumed by humans, resulting in toxic effects on human health (Xu et al. 2020).

After observing nanopollution effects, the scientist starts studying the introduction ways of NPs to the soil, its accumulation, and migration. A pathway to enter to soil is through the atmospheric precipitation, another one is by the sedimentation in the form of dust and aerosols, also direct soil absorption of gaseous compounds and the last one for the abscission of leaves, and most of them could be the product of anthropogenic activities. Nonetheless, a source of NPs is nanotechnology remediation, which is responsible for discharging many NMs into the environment while is used to remediate polluted environments (Rajput et al. 2020a, b).

In humans beings, also is studied the pathways of the entrance of NPs to the human body and consider that one of the principal ways is through the food chain, once the NP is in the environment, can be captured, metabolized, and transformed by plants and some small animals which are part of the food chain of the human. As a measure of control the use of NP, in 2004, it was established the Nanotechnology Research Center (NTRC) by the National Institute for Occupational Safety and Health (NIOSH), the NTRC is in charge of address occupational safety and health concerns about using engineered nanomaterials released in the environment, but still, be insufficient to control and prohibit the use of these NMs (Gupta and Xie 2018).

The NP's toxicity depends on many factors as the source, durability, and feasibility, dimension, dosage, nonetheless important, the intake or exposure via different pathways. The parameters, which are important for the NMs´ toxicity, include the size, bulk or surface chemistry, mass, aggregation, and surface area. The NMs´ toxicity effects that have been observed in many studies are cytotoxicity, dermal toxicity, cardiovascular toxicity, hemolytic toxicity, and immune toxicity (Mazari et al. 2021).

It is mentioned that there exist two routes of NP's entry into the human body, exogenous and endogenous, the exogenous route, is when the NPs ingestion is direct form, from hand to mouth contacts in the workplaces, like factory workers, engineers, and scientist working with NPs or NMs. Nonetheless, can be ingested directly via food, as it was mentioned before, by drinking water, drugs, or drug delivery systems. In addition, NPs can be inhaled, and enter the respiratory tract and travel into the gastrointestinal tract. When larger particles (5–30 μm) enter this respiratory via, usually are deposited in the nasopharyngeal region, while smaller particles (1–5 μm) remain at the tracheobronchial region, via sedimentation. Both can be removed or absorbed by mucociliary clearance (Gupta and Xie 2018).

In the case of submicron, particles (<1 μm) and NPs (<100 nm) can penetrate the alveolar region, and the removal mechanism are not sufficient. These NPs remain in close contact with the alveolar epithelium, but once deposited, NPs cross the blood–air–tissue barrier and get through the bloodstream, and reach other target organs. Meanwhile, some NPs stays attached to the lungs indefinitely, leading to injuries and biological responses. Some effects lead to chronic effects as inflammation, exacerbation of asthma, metal fume fever to fibrosis, chronic inflammatory lung diseases, and carcinogenesis (Gupta and Xie 2018).

In the different routes of NP entry, the one that has received more attention is inhalation, and it has been considered as the main route, as was mention before the lung exposure to NPs can lead to pulmonary fibrosis. The oral entry is different, the gastrointestinal conditions as stomach acidic pH and the elevated ionic strength, are expected to affect the physicochemical properties of the NPs, leading to toxic side products. In the case of the dermal route, some studies indicated that the penetration through the skin is limited. Some of them remain in the outer layer of skin, presenting local effects, while others can reach a deeper dermal layer, and enter into the systemic circulation (Vardakas et al. 2021).

The CuO NPs have applications in many areas as medicine, engineering, and technology, applicated to different materials as catalysts, semiconductors, sensors, gaseous, and solid ceramic pigments. In the pharmaceutic industry, it is utilized in the production of antimicrobials for *Escherichia coli* and *Staphylococcus aureus*. Moreover, some studies about the toxicity of CuO NPs on human health find out that there exist two main entry routes as inhalation and skin exposure. In the Assadian E. et al. assay, blood lymphocytes were incubated for 6 h with different concentrations of CuO NPs, measuring different parameters as cell viability, ROS formation, lipid peroxidation, cellular glutathione levels, and mitochondrial and lysosomal damage. The results obtained showed decreasing cell viability due to the significant increase of intracellular ROS level and loss of mitochondrial membrane potential (Assadian et al. 2018).

The carbon nanotubes (CNTs) have been studied due to their toxicity to animal cells, it is believed that CNTs interrupts the membrane electron transfer, can penetrate the cell envelope and oxidate the cell components, and also had effects on the production of secondary products as dissolved metal ions or ROS. Studies indicate that functionalized CNTs are safe for animal cells, but raw CNTs or without functionalization showed toxicity to animal or human cells in moderate exposure. Nonetheless, many studies reported that CNTs are much more toxic than carbon black, and inclusive is more toxic than quartz for lungs, which are a serious health hazard in chronic inhalation exposures (Hassan et al. 2020).

Among the effects of AgNPs due to its particle size, are their cytotoxicity. AgNPs showed toxic effects on cell viability, lactate dehydrogenase (LDH) activity, and ROS generation, depending on NPs size, also in the same studies, it was reported, that the surface area, volume ratio, and surface reactivity can be changed with the particle size. Moreover, other parameters are involved in these studies, as sedimentation velocity, mass diffusivity, attachment efficiency, and deposition velocity of NPs on biological or solid surfaces. The studies in cytotoxicity report that when AgNPs are smaller particles, are harmer than the ones with larger particle size, 15 nm hydrocarbon-coated AgNPs can generate higher levels of ROS compared with 55 nm AgNPs (Akter et al. 2018).

Lately, it is studied the action and effects of ENMs that are injected into the human body for medical applications as cancer cells. As it was reported, the cellular absorption of NPs happens by endocytosis or phagocytosis mechanisms, when NPs is inside the cells generate the ROS and causes injury to the cells, causing antagonistic health effects. In addition, NMs could act as allergens during the early stages of life, affecting human health, causing allergic inflammation in later stages. Studies demonstrate connections between NMs exposure during the neonatal phase with increased asthma exacerbation, limited lung function, and coughing without infection. Epidemiological studies reported cardiovascular effects like changing blood coagulation, causing alternation in cardiac frequency and function (Kabir et al. 2018).

It had been studied in animal cells that CNTs and TiO_2 NP could induce tumors. ENM is toxic for fibroblasts and epidermal keratinocytes causing gene alterations or difficulties on protein expression. A study with human cells and cadmium telluride quantum dots (CdTeQD) interactions, reported toxicity to human hepatocellular carcinoma $HepG_2$ cells, altering mitochondrial morphology and structure. In addition, it is suspected the effects on mitochondrial membrane potential and cellular respiration, increasing levels of Ca and decreasing the adenosine triphosphate synthesis (Kabir et al. 2018).

The CeO_2 NPs are important in some areas as medical applications, cosmetic and polishing products, and also in fuel additives, it had been demonstrated that they present genotoxic effects. The nanosized CeO_2 (7 nm) induces intense DNA lesions and chromosome damage related to oxidative stress depending on the dosage of the NPs. In the case of CuO NPs, which have applications in antimicrobial textiles, paints, and plastics, and also as biocides. These NPs are observed to be highly toxic compared to other carbon or metal oxide-based NMs, and the CuO NPs exhibited severe DNA damage. Many other NMs such as Au NPs, Al-oxides NPs, TiO_2, Fe_3O_4, AgNPs, and SiO_2 among others had been studied for genotoxicity resulting in DNA damages, most of them due to their concentration and particle size present in different studies (Raja et al. 2021).

The graphene-based nanomaterials (GBNs) demonstrate significant potential for biomedical applications, including gene therapy, drug delivery, tumor therapy among others. GBNs applications look promising, but they are still one limitation to reach clinical practice is that after its intravenous administration, when GBNs meets blood cells, induces immune perturbations. In addition, it is observed somewhere else that graphene oxide (GO) in different forms has effects on primary human immune cell populations. In other studies using palladium NPs (Pd NPs) in long-term exposures (more than 60 days), it was observed that when Pd NPs enter the human body through intravenous injections, the side effect showed was the alteration the cytokine serum levels in rats, suggesting a possible impact on the immune system after long-term exposure (Ballesteros et al. 2021).

In recent studies, the drug delivery systems (DDS) have been improved for their use in drug therapies for cancer and other diseases, and many NMs have been used for these systems, including as was mention before de CNPs, liposomes, high molecular weight polymers, low molecular weight compounds, metals, and ceramics. With the increasing use of the NMs, the researchers had been focusing on cytotoxicity after using these DDS in clinical trials. Somewhere else, was studied the pathways of DDS NMs in lymphatic vessels, and their influence on lymphatic vessel tissue. It is known that NMs can enter the lymphatic vessels, migrate to the lymph system, and accumulate in lymph nodes (Kuroda et al. 2021).

The effects of NPs have been studied lately due to the illnesses that have been appearing nowadays, it seems that the NMs that were introduced to the environment, expecting to obtain bioremediation or other applications, have consequences, not only for the environment, also is affecting plants, which some of them are food crops for animal and human. Sometimes, these NPs are transformed into ions, which also are toxic to the environment and organisms. It still be a wide world to explore and study the NPs effects in all the environments and in its organisms.

3 Environmental Concerns Regarding Nanotechnologies

Recent advances in nanotechnology have impacted many areas, products, and devices of our daily life, such as the biotechnological industry and health care, i.e., nanostructured compounds have transformed all fields. Environmental pollution is a major issue nowadays in all industrialized, emerging, and developed nations. Several solutions exist to solve this issue; therefore, the use of nanotechnology in human and environmental care is a revolution (Aguilar-Perez et al. 2021).

Because of their excellent permeability, effectiveness, biocompatibility, and biodegradability, ENPs are commonly employed as nanocarriers. While the positive impact of nanoparticles, nanomaterials, and other modified or ENPs on agriculture is acknowledged, the negative impact on the environment is not. Due to their widespread use, these trending NMs have maintained their presence in the environment, resulting in degradation pathways, intervention, and maybe helpful or harmful impacts (Jogaiah et al. 2021).

Ecosystems are constantly stressed by rising industrialization, urbanization, droughts, population expansion, and so forth. NPs are suitable for solving daily problems because of their high efficiency, relatively cheap synthesis cost, and simple nature. However, NPs have considerable drawbacks, including propensity to aggregate (limiting adsorption capacity and selectivity), difficulties recovering from substrate (soil, water, or air), unpredictable environmental behavior, and toxicity to ecosystems and human health. In addition, NPs are still in the lab; therefore, commercial applicability is still onsetting because NPs commercialization is challenging due to operational and economic constraints. Besides, Workplace exposure limits for important ENMs and defined ENM management practices are lacking (Glisovic et al. 2017). The properties that promote toxicity and bioaccumulation are being studied further. The public is seldom informed about risk management, and the effectiveness of present regulations to prevent ENM contamination is debated. Considering the issues mentioned earlier, an appropriate expertise and information dissemination network is suggested to advance responsible nanotechnology implementation worldwide.

Nanomaterials in environmental applications raise the potential of nanoparticle contamination of the ecosystems. Nanomaterials are increasingly used in sporting equipment and industrial and domestic items, and therefore, all of this has heightened worry about nanopollutants in the environment (Lee et al. 2017). Nanocontaminants in soil pose a severe hazard to the soil, water, air, ecosystem, and human society due to their toxicity (Adhikari and Dharmarajan 2021). Therefore, these nanocontaminants affect soil ecology, agricultural yield, product quality, groundwater purity, and human health. If future problems want to be avoided, then we have to protect and preserve our ecosystem and ecology alongside to we must also design a safety policy for certain nanocontaminants.

According to the literature review published by Adeel et al. (2021), metal and carbon-based NMs may be hazardous to soil organisms, depending on the receiver species, exposure duration, dosage and technique, and particularly the NMs physicochemical qualities (type, size, shape, surface charge, surface functionalization, etc.). At this review, was reported that NMs' negative impacts are connected to their size and relative surface area.

In the future, when nanochemicals are widely used to protect food production from climate change or in products and devices used daily, we may anticipate a substantial rise in NMs in soils, water, and air, which will unavoidably disseminate into the environment and affect biodiversity positively or negatively. Large-scale usage of nanoagrochemicals requires a detailed risk evaluation that incorporates data from uncommon long-term toxicity studies. This preventive strategy is required, since soil decontamination takes time and increases the costs of arable land.

4 Risks of Nanotechnology to Human Life, a New Hazard

To date, the prediction of manufactured NMs in both soil, air, and water are uncertain. Some mathematical models indicate that for water sources, such as rivers, lakes, and seawater, the concentrations of NPs are presented in a wide range in mg L^{-1} for the NPs of TiO_2, Ag, CuO, and carbon nanotubes (CNTs). The authors suggest that when it comes to modeling, there are factors that influence the results, as: (a) modeling adjustments, (b) variability of data in surface waters from different countries and regions, and (c) differences in the distribution properties of the NMs for both freshwater and seawater. However, it is suggested that TiO_2 NPs are more abundant in aquatic systems, possibly due to high production for world-scale product manufacturing (Zhao et al. 2020).

Moreover, our environment releases natural NPs from volcano ash, forest fires, among others, nonetheless, the synthetic NPs, are produced and released into the environment in exaggerated quantities, due to the increase in industrial activities as textile, automotive, food industry, to mention a few. Vehicular traffic emissions, residues of medicinal products, residues of cosmetic products, personal hygiene products, paints, waste of electronic devices, among others. The final destination of these residues containing nanomaterials, is at the wastewater treatment plants, dams, agricultural and non-agricultural soils, and air. However, various publications have made it clear that the presence of NPs in the human body is a reality. Therefore, the

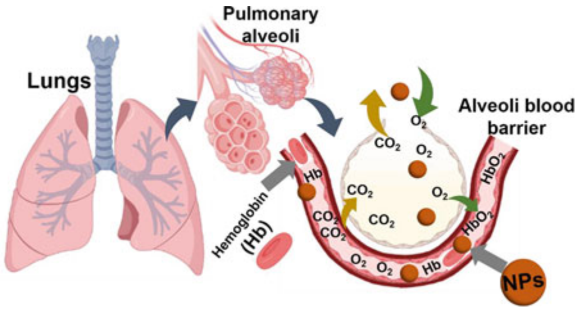

Fig. 2 Schematizes the movement of NPs in the pulmonary alveoli

uncertainty of human safety has to be considered seriously (Nasrollahzadeh and Sajadi 2019; Pérez-Hernández et al. 2020).

Therefore, due to air contamination with nanoparticles of both natural and synthetic origin, there is concern that NPs affect the epithelial cells of the pulmonary alveoli and consequently promote respiratory diseases in humans. The literature reports that, under normal conditions, the air can contain up to 10,000 microbes and fine particles of up to 50 μg per cubic meter. It is even a fact that the airways will exposure exposed to nanomaterials of micro or nano size (Nho 2020). Figure 2 schematizes the movement of NPs in the pulmonary alveoli during the entry and exit of carbon dioxide (CO_2) and oxygen (O_2) into the lungs, as well as the presence of NPs in the alveoli blood barrier.

Recently, reports indicate that the respiratory problem is caused by the industrial activities, such as the ceramics manufacturing. In a particular case, Martinello et al. (2021) demonstrate that when taken particulate matter samples in areas surrounding the ceramic factories in Santa Catarina province in southern Brazil, they observed NPs smaller than 10 nm. What was found in this study highlights the occupational risk when workers are in contact with nanometric material, which can represent health risks. On the other hand, Mexico City (MC) is one of the most populated worldwide, with an estimated air quality per year of 12 μg m^{-1} for PM2.5. With this information, and recognizing that more than six million vehicles and a little more than 50 thousand industries in operation per day. Indeed, the work of Calderón-Garcidueñas et al. (2019) estimated that adults (24 $\pm$ 9 years) in the urban area of MC presented around 22 billion magnetic NPs g^{-1} of ventricular tissue ($\sim$0.2 to 1.7 μg g^{-1} ventricular tissue) with a size of 15 nm. Other results indicated that NPs presented towards some organelles such as mitochondria and endoplasmic reticulum, while the crests of the mitochondria showed abnormalities in 3-year-old children.

In cities with populations of around 800,000 inhabitants, concern about air pollution is also present. For example, in Thessaloniki, Greece, when taking air samples, it was discovered that particles smaller than 14 nm within the particulate material corresponding to NPs of Fe_3O_4 and ferrites. The nasal cytologic samples of the residents corroborated that magnetic NPs are the ones that can most threaten the health of this population (Kermenidou et al. 2021).

In the process of trophic chains, the risk of human health is also in danger when there are NPs of Arsenic (As) present in the air in cities close to industrial areas. The works of Shahid et al. (2019) showed that with the foliar application of As on spinach (*Spinacia oleracea*), plants absorb up to 0.73 mg kg of As in the leaves, independent of the oxidative stress caused. Although, these values are below the critical limit (<1 mg kg^{-1}). Nonetheless, the authors suggest that monitoring of NPs in the air is worth close observation. In this way, it will be possible to avoid in the not too distant future, consuming plants with leaves contaminated with NPs.

In the soil resource, there are natural NPs, such as metal oxides and hydroxides (Al, Fe, Mn, among others), aluminum silicate (clays) or manganese (Mn), metal sulfides, enzymes, humic substances, viruses, and mobile colloids, among others (De Santiago-Martín et al. 2016). However, manufactured NPs and deposited in soil intentionally (soil remediation, soil fertility) or other unforeseen situations not are recognized by organisms (Khan et al. 2019). Therefore, once the NPs reach the soil, documented that in association with soils components, they undergo the bio/geo-transformation process, and consequently, dictate the bioavailability and toxicity of the NPs in plants and soil organisms, representing a potential threat to human health through the food chain (Rajput et al. 2020a, b). Zhao et al. (2020) reported that in the soil, the NMs of TiO_2 exist in higher quantity compared to the NMs of Ag, CuO, and CNTs for countries in Europe and the US. Therefore, the prediction of NMs in the soil cannot be generalized to other regions of the world. However, the authors suggest that the presence of NMs is lower in soil than in sediments and water. In particular, when we refer to agro-nanotechnology, the authors suggested that to increase the quality, production, and safety of crops, with the constant applications of nano fertilizers and nano pesticides, elements of nanometric size could be higher above the average. For example, the Cu, ZnO, and CeO_2 NPs at concentrations of 500 μg kg^{-1}, 16 μg kg $^{-1}$, and 4.3 mg kg^{-1}, respectively (Rajput et al. 2020a, b).

Due to the limited information on the effect of NPs on humans, in particular, in relationship with transformations that can occur in the digestive system, simulation work can be one of the first methodologies to understand the possible effects of silver NMs in the intestine in humans (Khan et al. 2021). In this line, with a simulated human gastrointestinal tract under fasting and feeding conditions, it was shown that both the synthetic silver sulfide NPs (s-Ag_2 S NPs) and the transformed NPs (t-Ag_2 NPs) present high stability in the simulated human intestinal tract. However, the transformed NPs presented a higher degree of transformation in the buccal phase concerning those existing in the stomach and small intestine. The authors suggest that both types of NPs may be accumulating in edible plants and consequently be subject to trophic transfer with high chances of reaching humans (Khan et al. 2021). In a similar study, was show that sludge contaminated by sulfurized Ag NPs (AgS NPs) can be transferred in the food chain since experiments with ryegrass (*Lolium perenne* L.), plants grown in pots with sewage sludge for 49 days, presented an accumulation of up to 0.2 mg kg^{-1} of Ag S NPs, while the phytophagous snails (*Cantareus aspersus*) exhibited bioaccumulation of Ag S NPs after 5 weeks. The authors suggest that there may be a high possibility that Ag S NPs transferred in the food chain, including humans, due to the practices of using sewage sludge in agricultural fields (Courtois et al. 2021).

In addition, during the soil nanoremediation process, there is concern that residual nanoparticles may reach humans through the food chain. However, when is applied the zero-valent iron nanoparticle (nZVI) under the soil surface, the authors suggest that it is an unlikely risk to humans due to mishandling of the material, even considering the risk during production, transport, or application (Grieger et al. 2019). Nonetheless, there is limited information on the impact and interaction of nZVI on cells and subcellular structures and the genetic effect of the cell (Sribna et al. 2019). In this sense, Sribna et al. (2019) verified that oocytes from mouse ovaries and follicular cells exposed to nZVI for 6 weeks suppress the formation of the polar body in oocytes (metaphase II) under conditions of experimental immune complex-mediated failure. In another study with albino rats, Akhtar et al. (2020), after peritoneal administration of $CoFe_2O_4$ NPs, was observed increased bilirubin and other liver function tests, as aspartate aminotransferase (AST) and alanine aminotransferase (ALT) compared to the control.

Using human umbilical cells, Coccini et al. (2020) demonstrated by flow cytometric evaluation that the exposure of Fe_3O_4 NPs between 2 and 8 days reduced the number of differentiation proteins β-tubulin III (β-Tub III), microtubule-associated protein 2 (MAP-2), and enolase (NSE) at 25 μg mL^{-1} 50 μg mL^{-1}. Likewise, using human cells of the SH-SY5Y line, Tahaei Gilan et al. (2019) demonstrated that nZVI intervenes in the rate of α-synuclein fibrillation (they shorten the delay and the fibrillation phase). Furthermore, studies showed that nZVI increases the propensity of α-synuclein for amyloid fibrillation, i.e., it can cause amyloidosis, a chronic disease involving the disorder protein metabolism. Therefore, the authors suggest that naked NPs can lead to a disorder in the rate of protein fibrillation. Other reports summarized damage to human and animal cells in Table 1.

Several NMs have studied water decontaminate contaminated with toxic organic and inorganic compounds and heavy metals. Studies show that Graphene, TiO_2, nZVI, nanofiber material, Ag, CNTs (SWCNTs and MWCNTs, principally), and a combination of nanomaterials are highly effective in removing or degrading contaminants. However, is required an adequate and safe strategy after using the nanoremediation technique. The literature suggests that it is of utmost importance to carry out rigorous and holistic studies to describe and understand the relationship between structure-functionality of NMs concerning their fundamental chemistry, i.e., know the functionality and toxicity (Saleem and Zaidi 2020a, b). In this sense, although there is too much information on the evaluation of NPs on aquatic organisms (plants and animals) under controlled conditions, exist limited information on the accumulation and magnification of NMs at trophic levels, including humans. In this sense, Xiao et al. (2019), in Lake Taihu, China, found Ag and Ti NPs with average sizes of 30 nm and 81 nm, respectively, being the Ag NPs with higher potential and bioaccumulation factor than Ti. As mentioned above, sludge and sediment are reservoirs for NMs. For this particular study, it was no exception where sediments from Lake Taihu are the principal source of exposure for aquatic

Table 1 Effect negative of NPs on human and of animal cells

Nanoparticle	Size of particle (nm)	Cells	Effects	References
CeO_2, CuO and ZnO	<25, <50, and <100	Human intestinal cells (Caco-2) and normal human liver cells (HL-7702)	At high concentrations (0.665 μmol L^{-1}) of the three NPs, for intestinal cells, necrosis, and decreased cell viability, a significant increase in ROS levels and a decrease in cell villi were observed. For liver cells, was no damage, even at high concentrations	Li et al. (2020)
CeO_2, SnO, Al_2O_3, and ZnO	9, 6, 51, 32	Human red blood cells (RBCs) and human skin cells (HaCaT)	At high concentrations of the four NPs (250 μg mL^{-1}), the authors observed enhance of hemolysis and decreased cell viability	Subramaniam et al. (2020)
SiO_2, TiO_2, TiO_2 P25, ag NPs, and polyacrylic acid (PAA) coated cobalt ferrite NPs	20–50, 80–400, 10–50, 10–30, 10–20	Human neuroblastoma cells (SH-SY5Y)	At high concentrations in all NPs (100 μg mL^{-1}), decreased cell viability	Lojk et al. (2020)
TiO_2	20	Rats corneal endothelial cells	Decreased cell viability, increased the content of lactate dehydrogenase (LDH) content, ROS generation, increased apoptosis, and cell cycle arrest. Concentrations of 100 μg mL caused more damage compared to 50 μg mL and control treatment	Yang et al. (2021)
CdS	5–9	Liver sample	The accumulation of NPs in the liver caused damage to liver function, damage in the liver, weight loss in individuals, among other indicators of oxidative stress at concentrations of 10 mg/kg of body weight compared to untreated organisms	Rana et al. (2021)

organisms. The findings were of concern, as the trophic magnification factors (TMFs) in invertebrates and fish species were 1.21 for Ag NPs and <1 for Ti NPs. This research confirms that in aquatic systems, the movement or transfer of NPs is realistic, and we as humans may be consuming shellfish contaminated with one or more NPs.

Based on experiments using model organisms has been presumed that silver nanoparticles may be dangerous to humans (Tortella et al. 2020). In fact, the review by Tortella et al. (2020) presents an interesting summary of the toxicity of Ag NPs in human cells and animals (aquatic and terrestrial). Of this review, it is striking that research shows that both coated or naked Ag NPs cause a decrease in the cell viability of human cells: dental cells, dermal cells, bronchial epithelial cells, intestinal epithelial cells, colon cells, among others. In addition, it summarizes the adverse effects in nematodes, worms, arthropods, insects, and some species of fish. Also, in the review by Baranowska-Wójcik et al. (2020), several cases of toxicity presented where after exposure of the TiO_2 NPs in rats (model organisms), whether by the oral route, or inhalation, the NPs accumulate in different organs, such as the digestive tract, heart, the kidneys, among others.

In agronomy, plants fertilized with nanomaterials to increase product quality or decrease plant toxicity in soils contaminated with heavy metals can have an impact on human health. For instance, to demonstrate the effect of the TiO_2 NPs (foliar application) in reducing the toxicity of Cd in Cowpea (*Vigna unguiculata* L.), the foliar applications of TiO NPs (six applications, in a period of 21 days), plants showed an increase in the chlorophyll content. However, the Cd content in the leaves and seeds remained above the permissible threshold. The results suggest that the daily intake of seeds with Cd exceeds that recommended by the WHO. Therefore, even the TiO_2 foliar application in plants contaminated with Cd can represent risks to human health (Ogunkunle et al. 2020). In another case, in aspects related to the trophic transfer of NPs from plants to cellular tissues in humans, Li et al. (2020) showed that plants treated with the three NPs absorb oxides of Ce, Cu, and Zn, which can cause significant damage to intestinal cells after oral exposure.

On the other hand, in the food industry, synthetic amorphous silica (SAS) has been used as an additive to reduce the caking of food powder. In the works of Hempt et al. (2020), through simulation studies, the findings demonstrated that of 10 SAS food-grade materials, a dose range of up to 50 μg ml^{-1} and during 48 h of incubation, none of the materials induced adverse effects on the cells of the human colorectal adenocarcinoma cell line (Caco-2). The results suggest that these materials do not represent a danger, at least on intestinal epithelial cells.

Considering the latest review articles (Pérez-Hernández et al. 2020; Singh et al. 2021; Seleiman et al. 2021, to mention just a few), the authors discuss the effectiveness of nanotechnology in the agricultural area. In fact, the authors are summary a list of positive and negative effects of various nanoparticles on edible and inedible plants. In most of these reviews, they highlight that the effect of nanomaterials depends on the properties of NPs, plant characteristics, evaluation time, concentrations evaluated, and, above all, the plant growth media, highlighting that the results are not the same obtained in Petri dishes compared to pots. Also, most researches are carried out in the early stages of plant growth.

In conclusion, the future of nanotechnology in several sectors is still uncertain, and even more, the trophic transfer of NPs in humans, which the mechanism of action is still unclear. For the above, an effort is necessary to dispel any doubts about the toxic effects generated in model organisms (plant and animal). These can be achieved with field experiments, considering that the Investigations have to be with a holistic perspective, i.e., consider climatic factors, soil properties, availability of nutrients, soil organisms, age, and type of plant and animal. On the other hand, with the increase in industrial activities, the production of consumer products based on nanoparticles, the increased traffic of vehicles, the increase in nanomaterials for soil remediation, among others, possibly the concentrations of NPs will be above the permissible limits in aquatic, terrestrial environments, and air. Besides, it is necessary to apply environmental reforms that indicate the maximum or minimum concentrations of NMs in products and environmental policies that promote the separation and ways of the liberation of products.

5 Life Cycle Assessment of Nanomaterials

In life cycle assessment (LCA) studies is important to know the origin of the nanomaterials (NMs) or nanoparticles (NPs), for determine the factors in inventory and give them the appropriate weight of impact, many industries have been utilizing green synthesis for decrease environmental impacts, helped for LCA. NMs had been studied since 1850 with Faraday but no one had studied the effects over other materials, environment or human health. With LCA can be determined the best option of synthesis methods, bioinspired methods in case of mining extractions are the best option. The best use of NMs is in medicine, food, agriculture and pharmaceutics, one of the most important factors to LCA study is the characterization factor to categorize the impacts and it could insert in data bases or models pre-established like USEtox criteria (Barik et al. 2021; Temizel-Sekeryan and Hicks 2020a; Committee et al. 2018).

There are very useful NMs, however, the released into the environment need to be quantifiable during production, transport and final disposal, studies show several models to predict the release and must be integrated to LCA, the economic model needs to be integrated too. The predict environmental concentration (PEC) calculation is very important to determine the impact and risk in atmosphere, water and soil, the data must be available in order for the industries that producing NMs (Giese et al. 2018).

The people need to know where are come from NMs and where are go to all the NMs, because there is a concern in the collateral effects that comes with the use of them. In Benjin China, were made studies from the perception of the indicators of the pollution and its monitoring impacts, the results of these studies is mainly for improve the monitoring systems because of its impact in the dairy society life, it is necessary to reduce the gap of knowledge that evaluates each stages of LCA (Liu et al. 2021; Salieri et al. 2018).

Robust LCA will provide valuable information, in the best of the cases new information from it can develops new ways to synthetize nanomaterials, and could integrate not only cradle-to-gate unless synthesis-to-product manufacture and end of life-to-use (Giubilato et al. 2020).

Sustainable development involves the balance of environment, economics, and social issues. The LCA needs to take these three criteria for analyze the product or the problem. One example of this kind of studies said that in the LCA cradle-to-gate in zero valent iron NMs the human health had the most weight of impact then the ecosystem quality according to the production and synthesis, the study shows that the milling and hydrogen gas methods were the most sustainable (Visentin et al. 2021).

LCA studies can be a tool for environmental issues, cradle-to-gate in treatment for water, that is in fact one of the most important issues to solve, showed that NMs can be used with other materials for make the best treatment and there are not much information about inorganic/organic nanocomposites LCA studies, this study showed the better option for remove Cu^{2+} ions from water is the method that involved the simultaneous deposition of poly-electrolyte complex (Barjoveanu et al. 2020).

Is important to knows all the risk in all the LCA stages (production, manufacturing, use end of life, release or recycle), those risks may be in the inventory box for determine its weight in the study, because in each stages, there are transformation and wastes, and is why need utilizing different models to simulate all the stages for calculate PEC that is the most important goal of LCA (Wigger et al. 2020).

Nanotechnology application is resent in a very wide fields of study, European Union are concern about the collaterals effects and these concerns been transformed in legal issues that register the entry of NMs in any product, there are legislation but it is short in comparison of the wide open information that cannot be included (Pavlicek et al. 2020).

There are many metal oxide nanoparticles that are been used in many fields like medicine, agriculture, etc., but is not very common to show how impact in the human, animal, soil. Large-scale manufacturing needs to be studied because it is necessarily known where the final disposal of those materials is. The most used metal oxide NPs are made of ZnO, TiO_2, Fe_2O_3, CuO because of their properties (Zhu et al. 2019). TiO_2 NPs are wide used in many fields, is important know how is their impact since the production to the end of use or deposal, many studies shows that the toxicity of this material is about their size of the NP in fact the decrease of size increases the toxicity in living organisms for example, hepatotoxicity, ZnO in soil dissolves very quickly (Hou et al. 2019; Saleem and Zaidi 2020a; b).

It seems the LCA in most of the cases limits to cradle-to-gate or gate-to-gate, however, is important to know how NMs affect in large time human health to include that information in LCA studies, the nine worldwide use of NMs are carbon black, synthetic amorphous silica, aluminum oxide, barium titanate, and the most used metal oxide and metal NPs, they cause pulmonary inflammation, heart rate variability, accumulative in blood and many others issues (Schulte et al. 2019; Yuan et al. 2019).

For example, Ag NPs have antimicrobial, electrical, optical, etc., properties and are been use in several fields, that is why very important make LCA studies mostly in synthesis process, a cradle-to-gate study shows that the physical methods have the lowest environmental impacts, the manufacturing of this NPs es about 50% of all of the NPs manufactured in 2017, so is important to take chance of this important studies for further improve systems and calculate PEC (Temizel-Sekeryan and Hicks 2020b).

Carbon NMs have a very important applications, these materials have been made by several methods, electrospinning fabrication uses state electricity with a high voltage. CNMs growth uses gaseous or vapor materials to react at gas phase or gas solid, sometimes this method uses benzene and high temperature. Template synthesis uses hydrolysis and calcination, is why very important implement green synthesis, because their applications in energy are very important for example their use in batteries, another important use is in electronics in where LCA can be used for reduce the impart to the environmental and apply green synthesis of materials or use methods with low temperatures combined with a good plan of release the materials in the end of the use life. (Zhou et al. 2020; McNulty et al. 2020).

CNMs, are being made for several methods, bottom-up is one of them, carbon dots made by carbon base NPs with luminescence properties have several applications, however, is important to know the Life Cycle Assessment for guarantee their sustainable production. The LCA in production method bottom-up shows that the use of microwave have less impact than hydrothermal synthesis because the electricity has the highest contribution (Sendao et al. 2020). Multiwalled carbon nanotubes (MWCNTs) are used for a wide fields of study, a LCA cradle-to-gate and gate-to-gate was made for the use in electrical membrane-like fillation conductive membranes, 20 years life time begin in manufacturing process to operate in the fillation process, the principal criteria took was human health, ecosystem and resources, this study demonstrated that the less concentration of carbon NMs is the best option (Ho et al. 2021).

Use LCA like a tool for achieve the process of NMs or the process to create new products with them is a goal, for example in energy creation source LCA promote the laser use to create biogas with the best cost-economics and reducing the impact in the production process. LCA like a valuable tool in energy generation give another use to animals waste with NMs (Samer et al. 2021).

The sea is the widest sink of waste from NMs, the Nanoremediation for this issue comes from LCA that can show the best choice because if not use this tool may contaminate more than help the marine environment. A study shows LCA cradle-to-final disposal in vivo and in vitro to compare the results of use of NMs (Esposito et al. 2021; Lead et al. 2018).

One of the most important knowledge is to know how use NMs to improve other materials or use those to remediate n a safer way, for example cellulose NMs can be a remediate tool for potable water, the conventional materials comes from activated carbon or petroleum have a large carbon footprint in their manufacturing to application process, biopolymer is the best choice by their biocompatibilities, biodegradable and low carbon footprint (Mohammed et al. 2018).

Risks in the food chain have also been indicated such as the carbon nanotubes (CNTs)-induced cancerogenic potential. To reduce CNTs risks to organisms need to make an LCA when the NMs will be used in products destinated to humans mostly (Jain et al. 2018).

It needed to use LCA studies to avoid the food waste, in this pandemic episode of the humanity, this tool can be useful to determinate the best way in food production, the principal stages must be nutritional, economic, and greenhouse gas (GHG) emissions, with this three axes the LCA study will be holistic (Aldaco et al. 2020). Even in medicals issues like a control of mosquitos that provokes many mortal diseases LCA could be a great tool to take the best option in the use of NMs technology for treatment and development of effective anti-malaria therapies or control mosquito vector (Borgheti-Cardoso et al. 2020).

It is estimated that only 20% of the manufactured NMs are studied in LCA from manufacturing-to-recycle or eliminate of the environment. The biggest release of NMs to the environment is during the use process, however, in each stage of LCA can be released NMs The exhaustive LCA in all the stages would be provide a wide information about the risk and consequences of use of nanotechnology, and the risks for the workers in the NMs industries whom are in constant exposure (Villamor Sancho 2020; Jiménez-Saborido 2021).

There is a long way to go in the study and analysis of the life cycle of NMs, however, it is important to start by gathering information and including it in the LCA inventories and in the simulation models to enrich the studies and make better decisions at the moment suitable. It is important to consider the three main axes of sustainability (society, economy and environment) when prioritizing risks.

6 Conclusions

Recent discoveries in nanotechnology have impacted the environment, health, agriculture, industry, and other fields. The NPs technology has significantly advanced the area and paved the way for future nanotechnologies. Although the significant influence of particle size on material toxicities has been established, the effect of particle size on nanoparticle behavior and reactivity is not well known. New concerns and thoughts regarding NPs need new laboratory approaches. NPs are now used in the environment to remove toxins from water, soil, sewage, and air. They have also been employed in environmental instrumentation, including sensors, green nanotechnology, and greenhouse gas reduction. Aside from their use, NPs may harm the environment from their manufacture through their disposal.

So, using NPs in remediation treatments is not a short-term solution. However, it is critical to study and assess NPs' environmental effect, interactions with live creatures, and their accumulation in ecosystems. Transferring the method from the laboratory to large-scale operation in treatment facilities is both costly and time-consuming. The limited and confusing legislation on using NPs for substrate (soil, water, and air) treatment and remediation restricts their use. Therefore, to meet the rising demand of NPs for several purposes, they must still overcome various challenges.

Risk evaluations of nanoparticles throughout their lifecycles are critical. The impacts of nanoparticles on industrial and non-industrial places are also highly relevant to scientific studies. Also, measuring people's exposure to nanoparticles from diverse sources is critical. It is suggested that more data be collected on diverse nanoparticles, notably their toxicological qualities. People should minimize exposure to artificial nanoparticles until new evidence has been reported based on long-life studies. Also, protocols for the safe handling and usage of nanoparticles in research labs, industry, agriculture, or environmental activities should be defined by competent authorities, organisms, or scientific commits. Finally, we must not encourage the use of nanoparticles in diverse domains until we have verified that their usage has no adverse consequences. Unfortunately, nanoscience and nanotechnology have delivered thousands of materials or devices worldwide without enough innocuity evidence.

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Integration of Eco-Friendly Biological and Nanotechnological Strategies for Better Agriculture: A Sustainable Approach

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1 Introduction

Agriculture serves as the foundation of the expanding economy, providing food for a better living. Agricultural production is currently confronting a variety of issues, notably unexpected changing climate, soil pollution with different detrimental environmental contaminants such as pesticides and fertilizers, and significantly rising food consumption attributed to the growing worldwide population. Healthy soils are the foundation for agriculture and the medium in which nearly all food-producing plants grow. Healthy soils produce healthy crops that in turn nourish people and animals. According to a recent United Nations Prospects, the world population will reach 8.5 billion by 2030 and about 9 billion by 2050, thus increasing the food demand. Thus, agriculture has a great challenge, which is to produce

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more with less, while confronting problems such as climate change and the limited availability of resources.

Soil contamination is a serious global problem; soil quality has deteriorated since the onset of industrialization and the development of agricultural practices. Pesticide use is haphazard and contributes toward pathogen and pest resistance, diminishes soil biodiversity, kills beneficial soil microorganisms, and causes pesticide biomagnification (Duhan et al. 2017). Nanoparticles are used in maintaining quality, fertility, and health of soil, they are synthesized as nanofertilizers and nanoherbicides, and these also ensure environmental safety. Nanotechnology is providing soil and plant nutrition with potential sustainable technologies, such as nanoemulsions, nanoagrochemical coatings, microencapsulation, and other active ingredients.

Crops are highly dependent on the availability of micronutrients and macronutrients in the soil, many of which are insoluble and not available to plants, and nanotechnological applications could play an important role in increasing, improving, and protecting crop productivity using nanomaterials, such as antimicrobial agents, nutrients, etc. Nanofertilizers improve efficiency and nutrient uptake in the plant, and they also ensure balanced nutrition of crops throughout the growth cycle. With the availability of nutrients to the crops, their protection from various pests is also necessary. Nanomaterial-based pesticides are used for its specific dose release to the specific crop plant, the loss of economic resources due to the diseases that different types of crops currently face. Need to be ceased or recovered and, some of them are seen showing antibacterial, antifungal, antiviral properties against the respective microorganisms are seen in use.

Sufficient quality of water availability is a critical problem in agriculture for crop output and nutrition. If sufficient water is not available, output will be hampered, and farmers would suffer financially (Lowry et al. 2019), for this remediation of water available that is contaminated is the need of the hour. Some external factors are responsible for affecting the growth of the crops that results into stress conditions for them. The stress can be divided into two groups: biotic and abiotic. Because crops are constantly exposed to a variety of stresses, it is vital to create techniques to increase resilience in order to ensure and improve food security. Because the fundamental objective is to expedite plant response to environmental challenges caused by biotic and abiotic variables, nanotechnology plays an essential role in crop management once again. (Kah et al. 2019; Shang et al. 2019).

Increasing rate of population demands increased rate of food production. The main cause of wastage and loss of food is spoilage of food mostly due to microbiological (fungal, bacterial, and viral) contamination. Food deterioration degrades food quality, impairs food security, shortens the shelf life of food goods, and increases the risk of food-borne infections illnesses. Alternative sophisticated ways for alleviating food shortages may be beneficial to enhance the amount of food available to a rising population, improve long-term economic performance, and reduce environmental impact. One of the most important safeguards against microbial diseases is food packing. Standardizing the process for the creation of novel compounds that act as food safety protection agents has received a lot of attention.

Nanoscience and nanotechnology are sophisticated techniques that are commonly used in the food business to decrease food waste and loss.

Despite advances in nanoscience and nanotechnology, the obstacles of long-term nanoparticle use to improve food quality remain unknown (Fortunati et al. 2019). To successfully provide nanotechnology, we must first comprehend the challenges of the agri-food production system

2 Nanotechnologies for Soil Management

Nanoparticles have received a lot of interest in recent decades as possible soil remediation agents all over the world because of their unique qualities, such as large surface area, high reactivity, and economic feasibility (Gómez-Sagasti et al. 2019). The possible effects of ENMs on soil ecosystem include: (i) affecting the germination of plant seeds, the development of plant roots and shoots, and (ii) influencing the growth of soil microorganisms and distorting the metabolism (Zhu et al. 2019; Chen et al. 2018).

3 Soil Fertility

The abundance of essential nutrients and minerals in the soil, as well as its aeration, water holding capacity, and texture, are all indicators of soil fertility. Fertilizers, herbicides, microflora, soil texture, pH, and organic matter are some of the factors that affect soil fertility (Javed et al. 2022). Chemical fertilizers greatly enhanced the agricultural production, but they have a number of negative consequences for the beneficial soil microflora, ultimately declining soil health. Most of these are inaccessible to plants due to run-off, resulting in pollution (Wilson et al. 2008). These issues can be remedied by employing nanoparticle-coated fertilizers. Nanoparticles have a higher surface area which can help with the progressive release of fertilizers by holding the material more securely for the plant. Moreover, nanocoatings provide surface protection for larger nanoparticles (Brady and Weil 1999; Santoso et al. 1995); eradicating weeds is necessary for soil health conventional means for the same are time consuming. Commercial herbicides eliminate weeds in the fields, but disproportionate use of herbicides over extended periods of time produces residues in the soil, which harm subsequent crop plants and pollute the soil, resulting in a loss of soil fertility. Nanoherbicides have the potential to remove weeds from crops in an environmentally beneficial manner, leaving no toxic residues in the soil or environment. These also ensure environmental safety (Duhan et al. 2017).

4 Soil Quality

Soil quality refers to a soil's ability to function within natural or controlled ecosystem limits in order to support plant production, maintain or improve water and air quality, and so on (Lori et al. 2022). Indicators such as organic matter content, salinity, tilth, compaction, accessible nutrients, and rooting depth aid in determining the health or state of the soil—its quality—in any specific location. There is mounting evidence that soil microbial diversity is a critical biological resource for ecosystem health (Wagg et al. 2021). Chemical pesticides and fertilizers, as well as innovative farm management practices and sophisticated equipment and technology, have enhanced crop yield-to-land-use ratios, but have also resulted in soil deterioration, chemical pollution, aquifer depletion, and soil salinity (Machado et al. 2022).

Oil pipelines are a major source of oil contamination in fertile soil, which has a significant impact on soil quality and necessitates efficient treatment. Surfactants' ability to solubilize and immobilize hydrophobic oil pollutants is appealing. For exthe removal efficiency of a silica nanoparticle stabilized ethanol–sodium lauryl sulphate surfactant was nearly 95% for hydrophobic silica-stabilized surfactant compared to only 75% for hydrophilic silica-stabilized surfactant, which was suggested to be the result of higher surfactant foam stabilization with hydrophobic silica nanoparticles (Ganie et al. 2021).

5 Decontamination

Organic pollutants such as pesticides, herbicides, and polycyclic aromatic hydrocarbons as well as inorganic contaminants such as metals (cadmium, Cd; copper, Cu; lead, Pb; zinc, Zn; mercury, Hg) and metalloids (arsenic, As; antimony, Sb) are the most common types of soil pollutants added from various sources such as military action, mining, road transport, and other agricultural, industrial, and domestic sources (Pan and Xing 2012; Pulimi and Subramanian 2016). These pollutants do not dissolve chemically or biologically, and thus, they build up in the soil over time, causing negative consequences (Baragaño et al. 2020).

Immobilization is one strategy that can successfully reduce metalloid toxicity in the soil by lowering the quantity of mobile and bioavailable portion of these pollutants in the soil by adding a potential agent to the soil via adsorption, ion exchange, or precipitation. Nanoremediation has the potential to lower the toxicity of soil contaminants (Medina-Pérez et al. 2019), they do soby immobilizing soil pollutants (Pb, Cr, As, Cd), converting more toxic heavy metals, Cr(IV), to less toxic forms, Cr (II), and degrading organic pollutants, such as chlorinated organics, DDT, pesticides, and herbicides, and nanoremediation has the potential to lower the toxicity of soil contaminants.

Carbon nanomaterials (CNTs, fullerene, C70, graphene, and others), metal oxide nanomaterials (Fe_3O_4 and TiO_2), nanocomposites, and other ENMs have all been utilized to immobilize inorganic and organic pollutants in soil matrix. Metal oxide NMs and other nanocomposites trap heavy metals and organic molecules by surface complexation, whereas carbon NMs absorb organic contaminants through van der Waals forces and - interactions. Heavy elements like Cd and As have a significant adsorption and immobilization capability in Fe_3O_4 (Qian et al. 2020).

6 Others

Nanotechnology can help develop more cost-effective and efficient water treatment and de-salination technologies, as well as renewable energy sources including highly efficient solar energy conversion systems (Wallentin et al. 2013; Wang et al. 2013). The intrinsic physicochemical features of the material, as well as the physicochemical parameters of the soil, influence particle dissolution.

7 Nanotechnologies for Crop Protection

It has been reported that agriculture is an area that currently uses a large amount of resources annually. Global crop production needs at least 2.7 billion cubic meters of water as well as millions of tons of fertilizers and pesticides (Kah et al. 2019). Currently, there is a major concern: the increase in world population and, as a consequence, the high food demand. It is estimated that by 2050, the population will reach 10 billion people, which will increase the demand for food by 50% (Usman et al. 2020). This problem is a global political, economic, and social concern that can be reflected in the UN Sustainable Development Goals and its 2030 agenda, where the second goal "zero hunger" seeks to achieve global food security and promote sustainable agriculture. Thus, agriculture has a great challenge, which is to produce more with less, while confronting problems such as climate change and the limited availability of resources. At this point, nanotechnology as an emerging area has multiple applications that allow it to explore different areas and one of them is agriculture where nanotechnological applications could play an important role in increasing, improving, and protecting crop productivity using nanomaterials, such as fertilizers, antimicrobial agents, pesticides, herbicides, nutrients, etc.

8 Crop Nutrition

With the current environmental problems, crop soils are deficient in nutrients, which affects the health of this system, its quality, productivity, and, therefore, economic losses for farmers (Chugh et al. 2021). Crops are highly dependent on the availability of micronutrients and macronutrients in the soil, many of which are insoluble and not

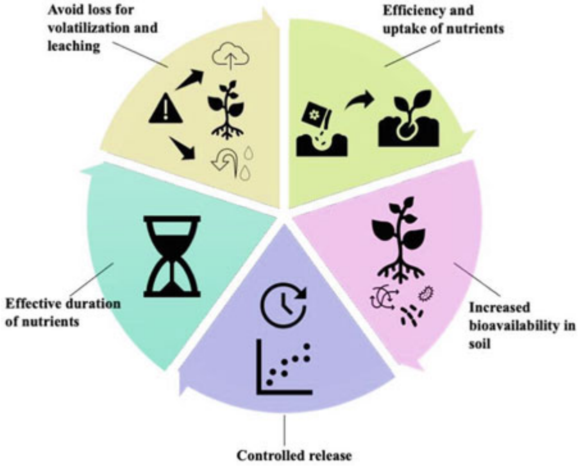

Fig. 1 Advantages of the properties of nanofertilizers in crop nutrition

available to plants. In fact, today, it is impossible to obtain adequate quality and nutrition without fertilizers (Marchiol et al. 2020). According to the International Fertilizer Industry Association (IFIA), global fertilizer consumption has increased significantly (Shang et al. 2019). However, applying chemical fertilizers has an effect on agroecosystems, such as damage to soil health and its microflora; in addition, inefficient fertilizer release causes environmental pollution in water bodies (Chugh et al. 2021) due to volatilization and leaching losses. In this context, nanotechnology is used to reduce these losses and develop controlled-release fertilizers to improve nutrient availability as it offers the potential to promote the nutritional status of crops, reducing production costs and contributing to the development of sustainable agriculture (Usman et al. 2020). This is because nanotechnological materials have specific and unique properties, such as size, high solubility, mobility, and surface area; thus, they can be applied and be very selective and specific, as well as release material in a controlled manner and combat nutrient deficiency.

The most widely used method for the incorporation of nutrients as nanofertilizers is the application to the soil, where several factors play a role, such as pH, cation exchange capacity, soil moisture, texture, water retention capacity, etc., which have to do with the mobilization of the nanomaterial and the regulation of nutrients. Other methods for application commonly used are seed treatments and foliar application (Chugh et al. 2021). There are a number of advantages offered by the properties presented by nanofertilizers, as shown in Fig. 1. Nanofertilizers improve efficiency and nutrient uptake in the plant, increase the bioavailability of elements in the soil, and control the release of fertilizers; nanostructures allow adequate duration for the required release and avoid loss by volatilization and leaching (Marchiol et al. 2020).

A wide range of nanoparticles have been proposed for application in agriculture. A classification of nanofertilizers was made by Liu and Lal (2016) which is based on macronutrients, micronutrients, nanomaterial enhancers, and plant growth

Table 1 Overview of nanofertilizer classification: examples and effects

Nanofertilizer	Example	Effects	References
Macronutrients	Nitrogen as urea–hydroxyapatite montmorillonite nanohybrid composite	In *Oryza sativa* enhancement in crop yield compare to control	Madusanka et al. (2017)
	Phosphorus	Applied to soybean increased the growth rate and seed yield	Liu and Lal (2014)
Micronutrients	Zinc as ZnO MWCNTs nanocomposite	Increased the germination percentage, root and shoot lengths and enhance seed water uptake applied to onion	Kumar et al. (2018)
	Iron as nFe_2O_3	In greenhouse conditions increased root length and plant biomass of *Arachis hypogaea*	Rui et al. (2016)
Nanomaterial-enhanced fertilizers	N as nanozeolite–urea	Using *Zea mays* as model plant the results were plant growth and nutrient uptake	Manikandan and Subramanian (2016)
	Cu–chitosan	Enhanced plant growth and chlorophyll on maize	Choudhary et al. (2017)
Plant growth stimulating nanomaterials	Titanium as TiO_2	Applied to rice increased P uptake and plant growth without translocation to grains	Zahra et al. (2017)
	Multiple walled carbon nanotubes (MWCNTs)	Enhanced seedling vigor and biomass on *Ricinus communis*	Fathi et al. (2017)

stimulating nanomaterials. Some examples and applications of this classification of nanofertilizers can be found in Table 1.

In this way, nanofertilizers ensure balanced nutrition of crops throughout the growth cycle, which ultimately improves agricultural production. It is good to take into account that its improvement and efficiency in crop nutrition can promote farmers to use it (Shang et al. 2019). Currently, the United States, India, and Iran already have commercial fertilizer products based on nanotechnology, and some examples are: Nano-Green, biozar nanofertilizer, and Nano-Gro™ (Prasad et al. 2017). Thus, nanofertilizers present a greater efficiency in the use of nutrients, thus reducing the waste of applied fertilizer and encouraging the protection of the environment by minimizing cultivation costs and the efforts required for the recovery of contaminated sites (Singh and Kalia 2019).

9 Pests Control in Agricultural Crops

Crop protection requires, in addition to good nutrition, practices aimed at eliminating pests. According to Mondal (2020), one of the main causes that affect crop production as well as crop quality in agriculture is pests: insects, fungi, and bacteria. In

Table 2 Characteristics and properties of pesticides: conventional vs. nanotechnological products

Conventional chemical products	Nanopesticides	References
Fungicide (Trifloxystrobin 25% + Tebuconazole 50%)	Nanoformulated fungicide Trifloxystrobin 25% + Tebuconazole 50% against *Macrophomina phaseolina* better performance	Kumar et al. (2016)
Commercial atrazine product	Atrazine-loaded nanocapsules more effective against *Amaranthus viridis* L.	Sousa et al. (2018)
Methyl eugenol	Nanogel. Methyl eugenol encapsulated. Statistically higher insect capture than ME application alone	Bhagat et al. (2013)

general, for crop protection, conventional practices involve the application of large doses of herbicides, pesticides, fungicides, and insecticides (Shang et al. 2019). These pesticides can be classified into inorganic, synthetic organic compounds, and growth regulators (Singh and Kalia 2019). It is estimated that approximately 99.9% of the total amount of pesticides applied on crops is lost to the environment resulting in serious problems in the food chain and human health (Usman et al. 2020).

Thus, another application proposed by nanotechnology is the use of pesticides based on nanomaterials that can be released in specific doses and in a particular plant tissue. An example of this nanotechnology is the encapsulation of pesticides, which consists of covering the active ingredient or ingredient of interest with another material of nanometric size. These nanoformulations favor the persistence of the pesticide in the plant preventing them from being harmful to non-target organisms; in addition, their release can be controlled, which enhances activity in crops (Shang et al. 2019) (Table 2).

Other examples of these nanoparticles are: iron oxide nanoparticles, gold nanoparticles, silver nanoparticles, nanoaluminosilicate, silica–silver, copper nanoparticles, etc. (Mondal 2020). The reason for their efficiency is due to the fact that nanomaterials have a greater contact area between the nanoparticle and the surface of the tissue, where the product is applied. The antimicrobial activity of nanoparticles is well-studied against bacteria, fungi, and viral pathogens (Usman et al. 2020). For example, silver has been reported to possess antimicrobial properties that inhibit the growth of plant–pathogens in a dose-dependent manner. Similarly, silica, titanium, and copper have potential to control agricultural pests (Iavicoli et al. 2017). Thus, nanopesticides are a nanotechnological tool with great potential, since they reduce the use of chemicals that are related to risks and environmental contamination and also reduce water and energy consumption, because they are applied less frequently than conventional pesticides.

10 Diseases Control in Edible and Nonedible Crops

According to reported by Shang et al. (2019), annual agricultural crop losses amount to $2 billion due to plant diseases and pests. In terms of productivity, an average of 20–40% are global crop losses due to poor disease management and control (Zehra et al. 2021). Nanoscience seeks to develop novel devices that can provide low costs, real-time information, crop status, among other important parameters for farmers (Singh and Kalia 2019); today, nanotechnology plays an important role in disease diagnosis and management in plants (Zehra et al. 2021), since devices with point-of-care diagnostic nanometer technology system have been developed that have application in plant disease management (Singh and Kalia 2019). One such device is nanosensors that look to improve plant management against diseases (Shang et al. 2019); their principle is based on producing an electrical signal when in contact with any pathogen (Zehra et al. 2021).

As mentioned at the beginning of this section, since there is a global concern that implies the attainment of the objectives of sustainable development of the UN, it is of vital importance to be able to carry out the control of crop diseases, especially those that are edible. There are a variety of studies describing the different effects of nanotechnology products on disease control. For example, it has been reported that ZnO, CuO, and Ag nanoparticles eliminate the symptoms of gray mold in the fruit of *Prunus domestica* caused by the fungus *Botrytis cinerea* (Malandrakis et al. 2019); also, effects of MgO and CuO nanoparticles have been found in *Solanum lycopersicum* that allow controlling the disease caused by the pathogens *Phytophthora infestans* and *Ralstonian solanacearum* (Shang et al. 2019). Likewise, Ag nanoparticles are efficient against different types of pathogens. They have been seen to be used in defense against yellow mosaic virus in beans (Elbeshehy et al. 2015) and in conjunction with silica help to combat the fungus *Podosphaera xanthii* in cucumber (Jagana et al. 2017). Sulfur nanoparticles exhibit antifungal properties in apple against the fungus *Fusarium solani* (Mondal 2020).

Antiviral effects of chitosan nanoparticles have also been observed in beans against *Bean mild mosai virus,* and in tobacco, against *Tobacco mosaic virus* (Malerba and Cerana 2016), the latter being a nonedible crop but important for the industry. Also rose showed effects when using a light-activated TiO_2/Zn nanoparticle composite to combat the bacterial disease *Xanthomonas* spp. (Paret et al. 2013), and according to El-Shetehy et al. (2021), SiO_2 nanoparticles can induce disease resistance in *Arabidopsis thaliana* against the bacterial pathogen *Pseudomonas syringae* better than its counterpart $Si(OH)_4$ compound when applied directly to the plant. These data show that the application of these nanomaterials is an important tool for agroindustry and the food industry in order to avoid the loss of economic resources due to the diseases that different types of crops currently face.

11 Irrigation and Water Requirement

The supply of fresh and clean water is one of the greatest challenges for human beings due to its industrial use and applications, such as in agriculture (Dasgupta et al. 2017). It is estimated that the water requirement per person is gradually increasing and not too late, and there will come a point where there is no water availability for crop production being this an essential element for plants as they need it for nutrient transport and to avoid drought stress. In the area of agriculture, water availability is a key issue for crop yield and nutrition. If the necessary amount of water is not available, it is very likely to limit productivity and affect farmers economically (Lowry et al. 2019). In addition, irrigation systems play an important role in agriculture and many farming communities cannot avoid using contaminated water for their practices, especially those in developing countries. This affects not only the crop but also the soil and human health (Baker et al. 2017).

Therefore, new nanomaterials and treatment technologies can provide water of sufficient quality for agricultural productivity. Nanosensors, for example, are part of a "smart plant" system that would allow communicating crop needs in real time, in addition, their use would allow detecting the nutritional status of water in the fields, and, however, not much research has been done in this regard (Kah et al. 2019). It is likely that in future, there will be water delivery systems with greater precision and range that allow plant uptake, encapsulation of water to be released according to demand, among other applications (Baker et al. 2017). Many of these nanotechnologies take advantage of non-traditional water sources for agriculture (wastewater, for example) in water-scarce regions (Lowry et al. 2019). Due to the contamination it presents, nanoparticle treatments have been implemented for remediation processes and to be able to remove contaminants in order to obtain water that is potable or clean enough to irrigate crops (Baker et al. 2017). Because of the need to meet the global demand for water, contaminated water purification techniques have been proposed, and some of them consist of employing photocatalysis methods (use of TiO_2 nanoparticles, silver, and carbon nanotubes), desalination, nanostructured catalytic membranes, nanoadsorbents (carbon and heavy metal-based materials), etc. For example, magnetic nanoparticles are used to remove Arsenic V by adsorption. Titanium dioxide nanoparticles are used for the removal of pesticides and herbicides, while silver and silicon are commonly used in disinfection processes of water contaminated by bacteria (Mondal 2020). In this way, nanotechnology has a wide range of applications for water management that can be used to supply agricultural industry activities.

12 Control of Biotic and Abiotic Stresses

We use the term plant stress when there are external conditions that affect the growth and development of the plant. Stress can be divided into two groups: biotic and abiotic. Biotic stress is due to biological organisms, such as viruses, bacteria, fungi, insects, etc., that reach the plant and can cause problems or even death, while abiotic stress refers to changes in environmental conditions, either physical or chemical: salinity, sunlight, increased temperature, cold, and drought (Lowry et al. 2019) (Fig. 2).

Due to climate change conditions and the increase in anthropogenic activities that alter crop production cycles as well as drought events, etc., crops continuously face all kinds of stress; therefore, it is necessary to develop strategies to generate resilience to ensure food security and enhance it in the coming years in which food demand will increase due to population growth. In this sense, nanotechnology again plays an important role to achieve crop control, since the main concern is to accelerate plant adaptation to environmental stresses due to biotic and abiotic factors (Kah et al. 2019; Shang et al. 2019), which are estimated to reduce global agricultural productivity by approximately 50% (Lowry et al. 2019).

As seen previously in the subsection on disease control and pest control, it is extremely important to be able to combat the biotic factors that affect crop productivity: insects, fungi, bacteria, and viruses. Some metal oxide nanomaterials can control many plant diseases, and in addition, there are the nanosensors that allow measuring and monitoring crops to determine diseases and entry of harmful agrochemicals into their environment with the aim of improving plant health and

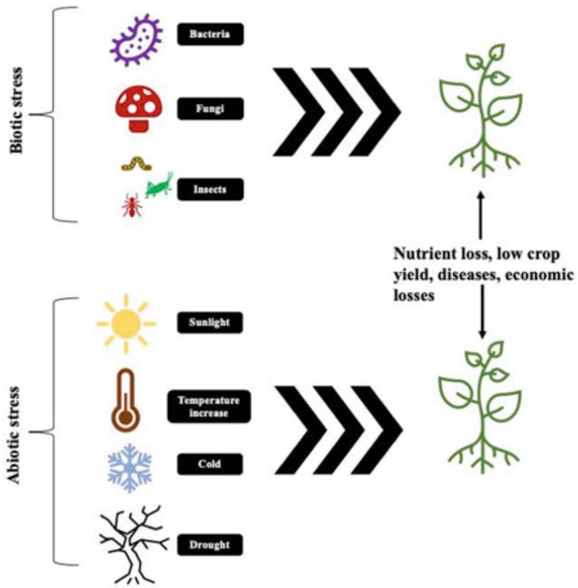

Fig. 2 Schematic representation of biotic and abiotic factors affecting yield, growth, crop nutrition, and economics in agriculture

nutritional quality and ensuring sustainable agriculture (Shang et al. 2019). Many studies are needed to know the mechanisms by which a crop can respond to stress conditions, since many changes are physiological and hormone-mediated. On the other hand, stress due to abiotic factors is challenging for nanotechnology. Salinity stress actually limits crop production; however, the use and application of SiO_2 nanoparticles increase germination and chlorophyll content in tomato under sodium chloride stress conditions. These same nanoparticles are effective under UV-B light stress in wheat (Siddiqui and Al-Whaibi 2014; Tripathi et al. 2017). Also, selenium nanoparticles help to combat stress. They have been reported to enhance antioxidant defense and promote sorghum yield under heat stress conditions (Djanaguiraman et al. 2018).

Also, devices such as nanosensors that act in response to stimuli are sought to be implemented. The aim is to deliver nutrient products when needed, provide a response to elevated temperature to manage heat stress, and implement techniques to modulate pH under necessary conditions (Lowry et al. 2019). Therefore, nanoparticles are a potential tool in the crop stress process that allows modulating biotic and abiotic stress-induced responses at different levels and different types of crops in order to ensure their safety.

With the above reviewed, we conclude that the use of nanotechnologies can improve the nutritional status of plants and promote crop yields, as well as tolerate stress, increase productivity, and control diseases and pests. In fact, nanotechnology makes us realize that the small could make a big difference in sustainable agriculture. For an adequate incorporation of the nanomaterial, more studies must be carried out, since several factors are involved: characteristics of the nanomaterials, application method, plant–soil–nanoparticle interaction, crop morphology, and physiology.

13 Harvest, Food Processing, and Shelf Life

The world population is expected to reach the figure of 9.7 billion people in 2050 and will increase the required rate of food production up to 60%. According to the Food and Agriculture, Organization of the United Nations stated that more than 1.3 billion metric tons of consumable food are lost or wasted every year throughout the supply chain, due to improper post-harvest techniques, packaging and storage techniques, shifting facilities of products to market. Improving the food production rate, it is compulsory to focus on the food wastage problem for the purpose to solve the food crisis caused by the increased rate of population and environmental issues. The main source for food loss and wastage is microbial (fungus, bacterial, and virus) contamination and food spoilage that decreases the food quality and affects food security, reduces the shelf life of food products, and enhances food-borne pathogens diseases. Moreover, the current global pandemic COVID-19 is also causing food crises issue across the globe (FAO 2020). Therefore, alternative advanced strategies might be effective to alleviate food shortages increase accessible food for a growing population, improve long-term economic performance, and decrease environmental impact.

Nutritionally essential agrifood products such as fruits and vegetables are substantially perishable and might not be accepted by customers for consumption if harvested product not properly managed. Moreover, fresh agrifood products play a chief role in trade at the international level after the globalization of business. That is why, the development of useful post-harvesting technology is to maintain the nutrient and taste value of fresh fruits and vegetables, hence reduces the loss of food by improving the shelf life of products. All the environmental stresses' (abiotic and biotic stresses) mechanical injury, causing adverse impact on fruits and vegetables, leads to shorten the shelf life of the product after harvesting (Shima et al. 2021). In addition, the respiration rate of fruits and vegetables is also inter-related with the reduction of shelf life, because a high respiration rate reduces the storage timing of products. Imbalance composition of various gases such as ethylene, carbon dioxide, and oxygen in fruits and vegetables drastically inhibited the ripening and another metabolic process resulted in food loss and wastage. Furthermore, notably characterized factors that are more than 90% humidity condition for storage of food provide a favorable environment for microbial growth to infect fruits and vegetables (Zhang et al. 2018; Grande-Tovar et al. 2018). According to the above-mentioned inhibitory impact on food products, suitable food packaging tools could play a fundamental role to prevent harvested products from microbial attacks, optimized the respiration rate and synthesis of ethylene hormone at the standard level.

In the agri-food industry, one of the most crucial steps is the food packaging that protects from microbial infections. Moreover, food spoilage represents a serious complication, harming human health. Therefore, researchers and scientists are focusing on standardizing the protocol for the development of new materials that serve as protective agents in food safety. The advanced technique known as nanoscience and nanotechnology is widely applied in the food industry to reduce food wastage and loss. There are two major types of nanomaterials (inorganic and organic nanomaterials) which produce by using two different approaches, i.e., top-down and down-up approaches, and the benefits of the food industry (Enescu et al. 2019). For that reason, emerging food packaging materials can increase the shelf life of the food to solve the global food supply problems. The application of nanoparticles in food packaging in various food industries tremendously minimizes spoilage of fruits and vegetables acting as a reactive oxygen species scavenger. In the food industry, these nanoscale materials extensively utilize due to high aspect ratio and surface area, improving the packaging quality, mechanical strength, thermal resistance, flexibility, barrier, and antimicrobial properties (Jamróz et al. 2019). Moreover, in nanofood packaging, there are three major types, such as improved nanopackaging, active nanopackaging, and smart nanopackaging.

14 Improved Nanopackaging

In the last few decades, nano-modified packaging materials show a promising source in the shelf-life improvement of agrifood products. The most widespread application for improving food packaging is edible nanocoating which enhances the antioxidant activity and extending the shelf life of agrifood products. Incorporating of nanomaterials onto the surface of the food improves especially barrier properties known as edible nanocoating. Edible nanocoating (combination of polymers and nanoparticles) could be beneficial by considering as a major obstacle, improve texture, flavor, and shelf life of food, and might be also acting as a semipermeable barrier for gases (CO, O_2) and moisture (Jafarzadeh et al. 2018). Due to the strong capacity of edible coating to prevent moisture and aroma loss, act as a barrier against oxygen penetration (prevent oxidative damage), researchers and scientists recommend edible nanocoating as a valuable tool to sustain the freshness of agrifood products for a longer period.

In an earlier report, (Emamifar and Bavaisi 2020) conducted a study to evaluate the nanocomposite coating impact on fresh *Fragaria ananassa* fruit. In this research work, they have developed a bio-nanocomposite (combination of sodium alginate and zinc oxide nanoparticles) and coated the outer surface of strawberry fruits at various levels for different storage intervals. Results demonstrated that strawberry fruit coated with a combination of sodium alginate and zinc oxide nanoparticles enhanced antioxidant activities, and reduced moisture loss. From this study, we may conclude that incorporated formulation of sodium alginate and zinc oxide nanoparticle coating might be a useful source to stimulate the antioxidant activity and enhance the shelf life of strawberry fruit for 20 days. In another report, Chi et al. (2019) investigated the effect of polylactic film nanocomposite comprising essential oil of bergamot, titanium oxide nanoparticles, and silver nanoparticles on the shelf life of mangoes. The overall findings of this study suggested that using nano-coated film containing essential oil, titanium NPs and silver NPs significantly act as a moisture barrier and considerably enhanced the shelf life of mangoes up to 2 weeks as compared to other applied coated materials.

The presence of oxygen in fruits and vegetable packaging can be considered as an inhibitor, causing many adverse impacts, such as loss of nutrients, fluctuation in flavor, color, respiration rate, and ethylene hormone synthesis process in agrifood products. Oxygen scavenger viable source against all of these antagonistic impacts and improves the shelf life of the product. Recently, various edible coated oxygen scavengers are extensively employing in the food industry to prevent products from spoilage by acting as a reducing agent (Chaturvedi and Dave 2020). The addition of nanoparticles in coating film accelerates gas barrier properties, decreases the respiration and transpiration rate, and alters the metabolic activity in fruits and vegetables (Chen et al. 2019). This study focuses on the impact of chitosan/cellulose nanofabric coating on the post-harvesting quality of strawberries, and Resende et al. (2018) successfully analyzed various parameters such as color, thickness, freshness, using electron microscopy, and water vapor contents to determine suitable formulation to coated strawberry. Results declared that strawberries coated with the highest range of CNF exhibited better response in reducing fruit mass, positive influence on color, maximum antioxidant activity, delayed oxidation process, and hence extended the shelf life of strawberry fruit. To improve the post-harvest quality of bananas, Li et al. (2019) employed soybean protein along with photosynthesized zinc oxide nanoparticle-mediated coated materials to check their role in the shelf life of fruits. Results suggested that SPI nanocomposite film considerably delayed ripening and weight loss of Banana and stimulated antifungal potential as relative to other coated treatments. This positive impact might be due to the oxidative stress-mediated antifungal mechanism of nanozinc oxide nanoparticles with the composition of soybean protein-coated material, scavenging reactive oxygen species, and consequently protect fruits from further spoilage.

After post-harvesting of agrifood products, the synthesis of ethylene hormone at an optimal level plays an essential role by increasing the life span of fresh fruits and vegetables. Overproduction of ethylene significantly accelerates the ripening process, chlorophyll degradation and ultimately causing spoilage of agrifood (Kaewklin et al. 2018). Semipermeable nanocoating materials are widely used to delay the ripening process in various fruits and vegetables, such as apple, mango, tomato, banana, onion, and carrot (Siripatrawan and Kaewklin 2018). These nanocoating tools decrease the concentration of O_2 in respiration and also involve optimizing the spreading of CO_2 from outside the tissue. The feasibility of ethylene scavenging action of edible coating (Siripatrawan and Kaewklin 2018) was developed chitosan incorporated with titanium oxide NPs to maintain the quality and improve the freshness lifetime of cherry tomato. They have monitored the variation in tomato weight loss, ethylene synthesis, and CO_2 rate in tomato sample coated with chitosan titanium oxide NPs film compared with another film (without NPs coated film) at 20 °C. The outcome of this study revealed that the formulation of chitosan titanium oxide nanoparticle film delayed the ripening process by slowing down the ethylene synthesis activity, hence improved the life span of cherry tomato. According to a recent report, the utilization of NP-based ethylene scavengers in the agri-food industry might optimize the ethylene production during the ripening process and consequently enhances the quality and shelf life of the product.

15 Active Nanopackaging

The main goal in improved food packaging is to develop nanopolymer materials that stimulate the gas barrier properties, resistance against high temperature and humidity, as well providing strength and flexibility to packaging materials. At present, the utilization of nanoscale materials in active packaging as an antimicrobial agent has a strong antioxidant activity that inhibits microbial growth. These nanoscale materials offer new plausible tools to improve food quality and safety (Mustafa and Andreescu 2020). However, selection criteria of nano-incorporated materials as an antimicrobial agent are based on cell wall composition of microbes and growth condition (humidity, temperature). Various bacterial and fungal microorganisms are mostly attacked on food to spoiled and inhibit the shelf life of products. To protect food from spoilage, nanoparticles mediated antimicrobial agents inhibit the metabolic pathways (macro- and micronutrient degradations), cell wall destruction, discontinuation of electron transport, and, as a result, stop microbial growth (Primožiˇc et al. 2021). Different nanoparticles (Ag NPs, TiO_2 NPs, zinc oxide NPs, MgO NPs, etc.) are widely using as antimicrobial agents in food packaging (Becerril et al. 2020). Titanium oxide NPs as non-toxic material are approved by European food safety to use as a food additive in packaging materials (Chaudhary et al. 2020). However, further research experiments are needed to understand the digestion and absorption of these nanoscale materials' impact on the human body to confirm either is it safe or not in the agrifood industry. Jasim et al. created plasticized polylactide composite film incorporated with silver–copper NPs and used in the packaging of the chicken meet to assess their antimicrobial activity. In this study, they were tested nano-based composite film against different bacterial strains (*Salmonella Typhimurium*, *Campylobacter jejuni,* and *L. monocytogenes*) in the chicken sample. Results declared that film containing silver–copper NPs exhibited the highest antimicrobial activity during 3 weeks. The created PLA Ag/Cu NPs composite can be employed in the active packaging of food products. In another report, buckwheat starch film containing zinc oxide NPs at various ranges (0, 1.5, 3, and 4.5%) was prepared and used in mushroom packaging materials to check their antimicrobial activity (Kim and Song 2018). Among all of the applied zinc oxide NPs, concentrations, buckwheat film containing 3% ZnONPs, tremendously showed antimicrobial potential against *L. monocytogens* and improved storage timing of mushroom. Recently, chitosan nanoparticles carried with essential oil of clove were applied by (Hadidi et al. 2020) to check their antimicrobial activity. Chitosan essential oil NPs showed maximum antibacterial activity against *L. monocytogense* and *S. aureusb*. From this study, we may conclude that chitosan NPs could effectively deliver a system in the active packaging of food products.

The above-mentioned earlier reports suggest that metal or metallic oxide nanoparticles incorporated with polymer matrix exhibited effective antimicrobial agents against microbes in food products. Therefore, nanotechnology application in agri-food industry significantly protects food items from pathogen attacks and hence improves quality and shelf life of products. In addition, high surface-to-volume ratio of NP-based antimicrobial agent also offers some useful features, such as thermal physiochemical, mechanical and optical properties to the food industry (Fig. 3).

16 Smart Nanopackaging

In general, smart packaging is defined as a promising technique that easily identifies the shelf life, food quality, due to its capability functions such as sensing, detecting, or measuring the microbial growth inside the food or surrounding environment of the product. Various biosensors have been developed based on a significant role such as

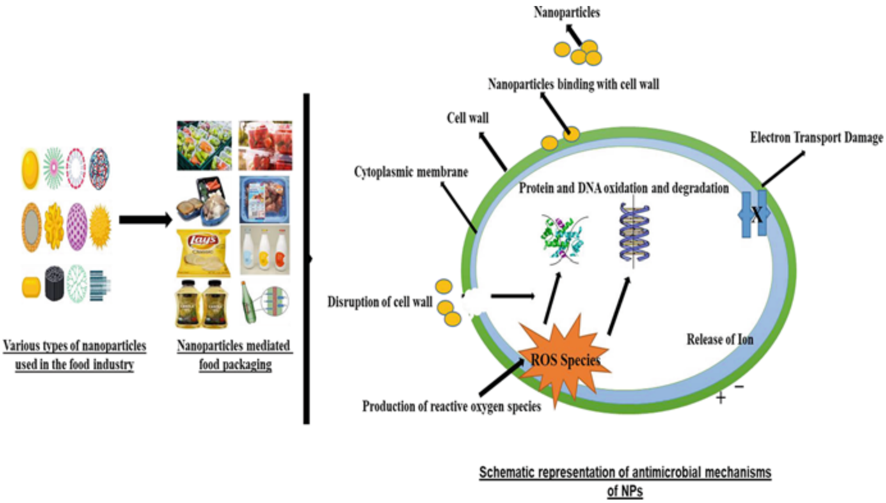

Fig. 3 Mechanistic view of antimicrobial potential of nanoparticle-mediated food packaging

food pathogen, identification, and environmental condition where products are stored, and freshness in the packaging (Jafarzadeh et al. 2020). Thanks to recent research in advanced technologies regarding fabrications of nanoscale components are utilized to make basic structural and function devices called nanobiosensors. These types of sensors are placed in food packaging to regulate the external and internal environment of food items. The main purpose of nanosensor employment in the food industry is to reduce pathogen detection time from days to hours or even minutes (Pramanik et al. 2020). Nanoparticle-mediated biosensors are highly marketed value due to unique optical properties, high surface ratio, and easy usage as compare to traditional biosensors. That is why, various nanomaterials are employing to make nanosensors and ensure food quality and safety and improve the functionality of packaging. Food packaging can be equipped with nanosensor which is sensitive to humidity, gas formation, and alteration in temperature. For instance, when foods are infected by microbes or gasses formation due to causing spoilage of food, hence, changes occur in packaging color, and finally, such changes notify a customer about this product is not fit for consumption. Nanosensor in smart packaging has great potential to response against certain chemicals marker, pathogen or other toxins in food and successfully monitor the freshness status, as well shelf life of the product. Various strategies (cyclic voltammetry, surface plasmon resonance, differential pulse voltammetry, interdigitated array microelectrode-based impedance analysis, amperometry, flow injection analysis, and bioluminescence) are using as nanobiosensors tools to quickly and precisely identify the different toxin, pathogens, toxins, and contaminants present in foods. Govindasamy et al. (2017a, b) developed electrochemical sensors by using gold nanoparticle-based graphene nanoribbons for detecting methyl parathion organophosphorus pesticide in fruits and vegetables.

Nanosensors used as freshness indicator give actual information recording food quality, started from storage processing and commercial exposition and must be sensitive to compounds known for causing spoilage, those coming from food spoilage or to microbial metabolites, such as toxins, that include volatile sulfides and amines, such as trimethylamine, $CO_{2,}$ and ethylene. Carbon nanotube sensors sensitive to CO_2, volatile compounds, and ethylene emissions have been the main approaches for detecting compounds causing food spoilage, and the achieved nanosensors proved abilities in providing the users with the exact scenario of food products freshness (Sharma et al. 2017).

During food supply chains, such as packaging, storage, handling, and distribution, thanks to time–temperature indicators (TTIs) are capable to screen the thermal history to determine suitable temperature to improve the quality and shelf life of foods (Priyadarshi 2019). In general, variation in food quality can be interlinked with temperature changes, indicated by the development of one or more colors. Wang et al. (2017) have been recently utilized gold nanoparticles in plasmonic thermal history indicator (THI), for evaluating the thermal history of fresh agri-food products. Nano-mediated plasmonic thermal history indicator showed that the exposure of fresh products to 40 °C changes the color from gray to red indicating the quality and shelf life of storage products.

To know about the actual status of packaged food, humidity indicators (HIs) are also essential to measure the moisture contents in the stored food items. By exploiting nanotechnology in the food industry, (Zhou 2013) developed nanocrystalline cellulose-based humidity indicators (HIs) for moisture determination in food products. In another report, carbon nanotubes (CNTs)-based sensors were employed in smart packaging by spraying carbon nanotube on the surface of packaging material. It was observed that CNT-based gas sensors exhibited an exceptional performance by sensing carbon dioxide and ammonia (NH3) gas in meat products (Bumbudsanpharoke and Ko 2015).

17 Safety to Nanotechnological System

As well-renowned, the application of various nanoparticles in the food industry has several benefits. However, at the same time, they also stance some serious complications to human health and the environment, due to their toxic impact (Gonzalez and Johnston 2018; Yang et al. 2019). In the last few decades, rising the application rate of nanotechnology in the agri-food sectors has fascinated public attentions. Recently, in many agri-food products, nanoparticles are either intentionally supplemented as food additives or unintentionally introduced via migration and arise some serious alarms due to their small size and interaction with cells. For instance, nanosize particles are capable to enter the skin and harm human as well as animal health. Experimental studies conducted by (He et al. 2018) have suggested that single- and multi-walled carbon nanotube can induce oxidative stress and fibrosis in the lungs of mice and rats.

To understand the exact mechanisms about how nanotoxicity influences human health and environment, we first have to clear concept regarding various exposure and migration routes of nanomaterials from the agrifood industry to the human body. Many processed food items bearing various nanoparticles are consumed by a human via intraoral, dermal, and pulmonary pathways. In addition, the main route for nanoparticle migration is the oral captivation pathway by which we intake, water, and nutrients, and thus, nanoparticles enter through the mouth to the stomach and then intestines, posing serious human health complications (Gupta and Xie 2018). The direct contact of nanomaterials used as food additives/as antimicrobial agents/as a nanosensor in food packaging might be threats to human health. The formation of reactive oxidative species (ROS) serves as one of the central toxicological mechanisms affecting cellular damage and ultimately cell death occurs. During severe stress conditions caused by nanotoxicity, over synthesis of oxidative species (ROS) leads that damaged DNA, neuron, autophagy, and aging-related ailments in humans. Moreover, the release of metal ions from nanoparticles also can produce adverse impacts such as allergic reactions after consumption of nano-mediated food products (Yu et al. 2020).

For nanomaterials toxicity evaluation, challenge overcoming for the model organism as zebra-fish used the maintenance and development for human and animal cell cultures. Rapidly reproducing ability is invertebrate fish, the European Union (EU) and U.S. Food and Drug Administration approved zebrafish model to evaluate the nanomaterials toxicity (Jeevanandam et al. 2019). Comprehensive analysis about to check nanotoxicity effect on Zebrafish alteration or mortality behavior suggested that nanomaterials do not cause developmental defects. However, investigation regarding bioaccumulation and distribution of nanomaterials proposed that they are present in a particular position within the body (d'Amora et al. 2018). While some other studies acknowledged that phytosynthesized zinc oxide nanoparticles have been carried out to check their toxicity in in-vitro and in vivo model, which demonstrating that green synthesis of nanoparticles is less toxic and more biocompatible capacity as compared to chemically synthesized nanoparticles (Shubha et al. 2019). However, some reports confirmed that the accumulation of nanomaterial in the human body is due to the utilization of nanopackaging or nanopressed food items (Abo-Elseoud et al. 2018).

That is why, risk assessment procedures should be thoroughly followed during the food processing industry. Even, through the advancement in nanoscience and nanotechnology, challenges for sustainable utilization of nanoparticles to improve food quality remain obscure (Fortunati et al. 2019). It still covers all the general aspects regarding nanomaterials used in the food industry. Therefore, scientific communities and organizations need to evaluate and reevaluate the specific nanoparticles' properties and their impact on human health. In many cases, there has been no standard protocol for the implication of nanomaterials in food items. According to the FDA statement, all food products comprising nanomaterials can be harmful with no further optimized procedure for their industrial application. On the other side, food manufacturer industries invested a lot of money for sustainable application of nanotechnology to get novel and safe nano-based products. To date, few nano-mediated (titanium oxide nanoparticles, iron nanoparticles, zinc oxide nanoparticles) food products have been approved as a food additive and antimicrobial agent in the agri-food industry (Xiaojia et al. 2019).

In the agriculture sector, nanoparticle applications show Hormesis impact (both positive and negative) on crop growth development and productivity. However, it depends upon type, shape, size, concentration, and, most importantly, the accumulation of nanomaterials in different plant parts. For example, optimal uptake and accumulation of NPs significantly accelerate the growth, while maximum accumulation causes nanotoxicity which drastically inhibits growth and productivity (Paramo et al. 2020). A recent report clearly described the accumulation of various NPs (copper, gold NPs) in the different edible plants, such as pea, sunflower, and wheat rice, and pumpkin (Mittal et al. 2020). These nanomaterials traveling via vascular tissues accumulate in various edible parts of crops, fruits, vegetables, which raises the question of whether the use of NPs in the agrifood sector is safe for consumers. NPs are transported using advanced applications such as nanopesticides, nanoinsecticides, nanofertilizer, nanoplant growth regulator, nanoremediation, and many encapsulated nutritive feed, and this feed is further utilized in aquaculture, livestock production, horticulture, poultry, food packaging industry, etc. Finally, these nanoscale materials move into the food chain and accumulated in the human body via consumption of food and eventually distresses human health (Fig. 4) (Kumar et al. 2020). Therefore, we need to understand the difficulties of the agri-food production system to serve nanotechnology successfully.

The importance of public awareness and acceptance is often overlooked by food manufacturers. In a real sense, most food manufacturers prefer to keep their new product development "buried" and not share it with the public (possibly due to competition and trade secrets). This may be incompatible with the public's desire to understand what and why the food manufacturer is marketing. According to a case study in Singapore, ignorance of nanotechnology and its adverse effects increases the public's poor opinion of nanotechnology (George et al. 2014). Even worse, another survey conducted on the island of Ireland (Handford et al. 2015), agri-food organizations (stakeholders) have a deficient awareness of nanotechnology. With nanotechnology in the food industry, public opinion is split into assent and dissent (or altruism and skepticism) (Brown et al. 2015). The public's reaction is highly dependent on the specific applications. According to a nationwide online survey in the United States, consumers are only willing to pay less for canola oil that is processed or packaged with nanotechnology modified seeds or techniques, and canola oil with health-enhancing nano-engineered oil drops showed no significant difference (Zhou and Hu 2018). The public appears to have a neutral attitude toward nano-engineered canola oil, even though nano-engineered canola oil does not contain all nanofood.

Protection to the biological entity (chiefly appraised from toxic data) is the initial apprehensiveness for all these current sequences. Even so, the concern of their possible effects on the atmosphere and natural ecosystems should be raised too. Our main compass is to apply nanotechnology and work out fresh products in the food industry. The number of marketing products has been accelerating in pamphlets

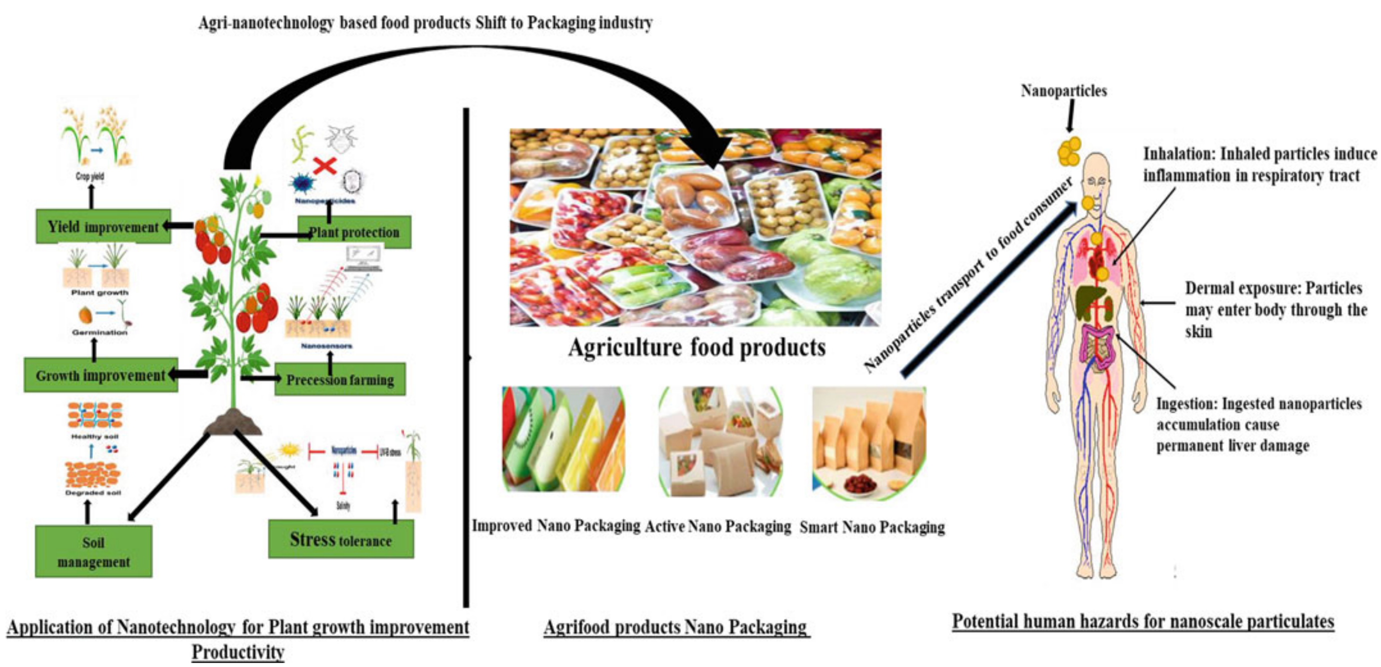

Fig. 4 Nanoparticles accumulation in the food chain and their impact on human health

every year. That makes administration and legislation more emergent. Whether new products can bear an eye view in the food market also depends on the collaborative carriage and consumers' acceptance. The main reason for this is that the general public has limited access to food nanotechnology information and resources. Nanotechnology is not yet a well-developed technology for use in the food industry. Due to a lack of scientific evidence, it is difficult, if not unethical, to publicize this unproven technology. Both government and industry face significant challenges in ensuring consumer trust and acceptance of nanotechnology-based foods available on the market. Appropriate labeling and regulations for the marketing of nanofoods should be recommended to increase consumer acceptance. As a result, if these nanotechnologies are adequately managed and regulated in agrifood sectors, and they can be beneficial.

18 Conclusions

Nanotechnology is a rapidly growing field in agricultural practices, with numerous applications. It is used in maintaining quality, fertility and health of soil, nanoparticles as nanofertilizers, and nanoherbicides, and ensures environmental safety. Nanotechnologies such as nanoemulsions, nanoagrochemical coatings, microencapsulation, and other active substances are providing soil and plant nutrition with potentially sustainable technologies. With improving efficiency and nutrient uptake in the plant, and they also ensure balanced nutrition of crops throughout the growth cycle. Nanopesticides are used for specific dose release to a specific crop plant, preventing pesticides from harming other crops. Contaminated water is remedied using nanotechnology, making it suitable for agricultural fields. Food spoilage is also prevented using nanoscience and nanotechnology, as they are sophisticated techniques used in the food industry to reduce food waste and loss. Food nanopackaging has received a lot of attention against microbial diseases. As a result, nanotechnology has a wide range of agricultural management applications that can be used to supply agricultural industry activities.

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