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Review Article

Bioinspired Advances in Nanomaterials for Sustainable Agriculture

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Rising demand for food production and an intensified usage of hazardous substances on the farmland are the driving force behind the emergence of green nanotechnology. Eco-friendly nanomaterials synthesised using plant sources and microorganisms are expected to catalyse a revolution in the agricultural sector by introducing nano-enabled smart sensors for metals along with organic toxins, supplying micronutrients; balancing the plant hormones, soil quality, and moisture content; stimulating plant growth; and minimising the usage of toxic chemicals by nanofertilizers and nanopesticides. As no single nanocompound has proved to be completely sustainable, this review discusses a wide variety of sustainable routes to implement nanomaterials to increase productivity, protect, and monitor crops through innovative nano-aided agricultural practices. Nevertheless, as the progress of research and commercialization in this area is still marginal, an understanding of complex dynamic behaviour, careful evaluation with targeted delivery of these compounds in the environment, and strong governmental regulatory norms are necessary to realize the effectiveness of green nanotechnology for sustainable agriculture. This article outlines some major advancements in recent years related to the implementation of eco-friendly nanomaterials in the agricultural sector. A systematic and comprehensive approach to adopting green nanotechnology would certainly promote a sustainable movement resulting in a beneficial economic and ecological impact.

1. Introduction

The most prevalent problem associated with the agricultural sector worldwide is the management of available natural resources in a sustainable manner. Despite numerous drastic technological innovations and huge capital investments which have successfully increased food production, the prevailing farming practices have a profound negative impact on ecological systems creating an imbalance in the natural cycle. Some of the ills such as depletion of soil productivity [1], soil salinization [2], soil moisture [3], soil organic matter [4], reduction of genetic diversity [5], creation of pesticide-resistant pathogens [6], and seeping of pesticides and fertilizers into groundwater [7] are increasingly being observed as barriers to sustainability. Many countries have attempted to increase the gross value of production through shifting towards perennial crops and expansion of usage of land. In view of these factors, a set of technologies acting as an engine of growth is becoming crucial to face the food production challenge without harming the environment.

"Green nanotechnology" often refers to the synthesis of nanomaterials by reducing or eliminating the use of harmful chemicals and harsh reaction conditions. The utilization of plants and microorganisms to generate nanomaterials has gained popularity owing to their genetic diversity and variety of plant constituents such as phenols and alkaloids that help metal ions to be reduced to the nanodimension through a concerted step. The shift of agricultural science towards the use of nanomaterials has revolutionized food production [8] through eco-friendly means of managing natural resources and has opened up new avenues in agriculture. Often referred to as "green nano agro science," this area of study has a great potential to implement the strong foundations of green chemistry and engineering into real practice of agriculture in an eco-friendly, simplified, cost-effective, scalable, and biocompatible route. This article focuses on some notable trends, such as the use of microorganisms and plant extracts in the development of green nanomaterials, which are globally renowned applications for pesticides. Herbicides, improving soil quality, soil moisture content, and detection of toxic metals and organic moieties for sustainable agricultural production systems, possess the competency of escalating the agro-output that has continued to be an unprecedented challenge for years.

2. Microbial Synthesis

Synthesis and application of biological nanomaterial, using microorganisms, offer a highly scalable, biocompatible route. Originating from biological sources, these eco-friendly microfactories offer a wide variety of bioremediative applications. Several approaches are available for microbial biosynthetic engineering among which bacterial synthesis, fungi, and yeast-assisted routes are the prominent ones as represented in Figure 1. Additionally, microorganisms have an edge over plant sources for nanosynthesis, as nanomaterials prepared using plant extract have a tendency to become polydispersed [9] caused by phytochemicals whose proportions vary with seasons. The shape, surface characteristics, bioavailability, homogeneity of size, and quality of NPs produced by microorganisms may, however, differ considerably from those generated by other methods.

2.1. Bacteria. Bacterial synthesis of nanoparticles has become highly popular due to the ability of bacterial cells to multiply vigorously under various pH, temperatures, and high concentrations of metals. The protein in the bacterial cell membrane functions as either ATPase or as chemo-osmotic or proton antitransporters facilitating the extracellular or intracellular production of nanoparticles. The benefits of probiotic microorganisms have been realized through the negative electrokinetic potential enabling the attraction of cations that often serve as the initial point of the biosynthesis process [10]. The mechanistic understanding of the process has led to many valuable metal nanoparticles such as colloidal silver nanoparticles using Lactobacillus [11, 12], gold nanoparticles using Lactobacillus kimchicus DCY51T [13, 14], and cadmium sulfide with the aid of poly(hydroxybutyrate) [15]. The environmental compatibility shown by these bacterial strains has shown a great promise and has inspired numerous researchers worldwide to explore other microorganisms for increasing crop production.

2.2. Fungi. The major distinction among bacteria and fungi is that fungi consist of larger proportions of proteins, which enable higher productivity of nanoparticles. Additionally, the use of fungi allows large-scale synthesis and well-defined morphology, because of the intracellular enzymes that trigger both intracellular and extracellular synthesis. Intracellular synthesis starts with the adhering of heavy metals to the fungal cell wall using proteins that act as enzymes that produce electrostatic interactions that are responsible for the movement of electrons leading to the reduction of metal ions. Recent developments in this regard include fungi that act as reducing and capping agents in the synthesis of gold [16], silver [17], and SnO_2/Pd [18] nanoparticles.

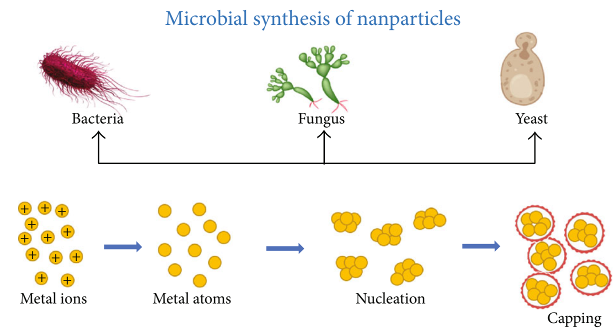

Figure 1: Microbial bioproduction approaches to green nanomaterials.

2.3. Yeast. Largely explored recently, these unicellular microorganisms with a wide variety of 1500 species assist the synthesis of nanoparticles with innumerable advantages. Despite the limitation of severe pathogenicity towards humans, fungal species are used to produce nanomaterials on a large scale using different incubating conditions, such as precursor resolutions and response time. The extracellular biosynthesis of AgNPsK and AgNPsU [19] with the aid of yeast strains of Pichia kudriavzeviiHA-NY2 and Saccharomyces uvarumHA-NY3, quantum dots of CdSe using tryptone-enriched media [20], and nano-AgCl [21] using commercial yeast extract are some of the classic examples. A nanomaterial with high stability can be achieved through an optimization of the inherited, genetic, and enzymatic properties of the chosen yeast and its cell growth.

3. Phytosynthesis

Plant mediation for synthesis is often termed "phytocatalysis" and is applied worldwide to the synthesis of nanomaterials. Vegetal constituents such as polyphenolic compounds, nitrogen-containing alkaloids, water-soluble diversified tannic acids, iridoids, highly nutritious secoiridoids, benzopyrone derivatives called coumarins, and isoprenoids together form a complex catalytic system exerting its action through chemical reduction or electrochemical reduction processes to produce nanomaterials. Nano-Ag particles [22] generated using extract of leaves from Alstonia macrophylla were found to be highly effective in transforming 4-nitrophenol to 4-aminophenol and p-nitroaniline to p-phenylenediamine. Bello et al. [23] also reported a similar reduction in 4-nitrophenol [23].

Although researched rarely, the gold nanoparticles find usefulness in catalysing the reduction of 4-nitrophenol

Table 1: Examples of plant-based nanoparticles, morphology, and applications.

Prepared nanometal	Extracted from plant	Size	Shape	Application	Ref
Silver	Alstonia macrophylla	70 nm	Spherical	Reduction of 4-nitrophenol and p-nitroaniline	[22]
Silver	Guiera senegalensis	50 nm	Spherical		[23]
Gold	Artemisia dracunculus	91 nm	Hexagonal and triangular	Reduce 4-nitrophenol	[24]
Palladium	Chitosan-tannin	6.01 nm	Spherical	Degradation of Congo red	[25]
Iron	Lagerstroemia speciosa	50–100 nm	Spherical	Degradation of methylene blue	[26]
Copper	Plantago asiatica	7–35 nm	Spherical	Cyanation of aldehydes	[27]
Ag/Au	Silybum marianum	40 nm	Spherical	Reduction of 4-nitrophenol	[28]
Ag/Fe	Palm date fruit extract	5–40 nm	Disks	Degradation of bromothymol blue	[29]

[24]. A comparatively widely used Pd nano [25] and popularly studied Fe nano [26] produced through plant extract used to degrade environmentally harmful dyes prove the unparalleled catalytic activity of plant extracts. The use of transition metals has been endorsed with Cu nanoparticles produced by the extract of *Plantago asiatica* [27] in a short time of 30–60 min. These particles within the range of 7-35 nm successfully completed cyanation of aldehydes with over 85% yield. Besides these metals, bimetallic nanoparticles have also been described such as Ag/Au [28] nanoparticles produced using seed extract from *Silybum marianum* which plays the role of a reducing and stabilizing agent. Ag/FeNP disks [29] with dimensions 5–40 nm were produced by palm date fruit extract which could degrade bromothymol blue dye via a Ag/FeNP/H_2O_2 catalytic system.

Numerous mono- and bimetallic nanoparticles are studied and reported with a focus on synthetic methodologies, characterisation, and novel applications, among which a few are listed in Table 1.

4. Why Green Nanotechnology for Agriculture?

With the increasing dependency on insecticides and pesticides and the concurrent awareness of exposure to these chemicals at small levels impacting the environment, there is a burning need for agrotechnology to shift towards greener technological systems to be implemented on farms. Implementation of nanotechnology in agriculture after rendering remarkable contributions is now a proven solution to move towards sustainability. However, many processes involved in the synthesis of nanosynthesis and application involve high temperatures [30], pressures [31], acidification [32], and toxic metals [33].

Hence, the last two decades have witnessed a tremendous change over in the approach to nanosynthesis from traditional methods to plant-based protocols due to many advantages such as sustainable pathway, diversified plant metabolites, advanced extraction and separation strategies, development of exhaustive phytoconstituent database, and instrumental aid extended by high-performance liquid chromatography-mass spectrometry, high-performance liquid chromatography-nuclear magnetic resonance, high-performance liquid chromatography-mass spectrometry, and centrifugal partition chromatography. Highly efficient extraction methods such as chemogenomics, metabolomics, coupled with ultrasound, enzymes, hydrodistillation, and supercritical fluid extraction have led to the preparation of customized extracts that were not feasible with traditional methods [34]. On the other hand, nanotechnology can be used in conjunction with these advancements to successfully achieve a sustainable agricultural system, and a large emphasis is therefore laid on plant-based nanotechnology formulations which have a great potential to solve major problems of farming.

5. Agro Applications of Bio-Based Nanomaterials

A group of agricultural practices, often referred to as farming, represents an open system with an easy exchange of energy and matter. With abundant public funding and considerable momentum, the agricultural sector has been considered an umbrella for nation development for decades. However, with the fast development of technology, the intervention of agrochemical agents and the lack of control over the input of toxic chemicals have become unavoidable.

With the advent and development of nanomaterials, precision farming has gained high popularity and is viewed as a remedial measure to many problems in farming. Combating insecticide resistance, soil moisture balancing, nanoparticle-mediated gene or DNA transfer in plants, food processing, increasing shelf life, treating agricultural waste, reducing spraying of pesticides, plant breeding, and food packing are some of the areas where nanomaterials are expected to play a vital role. The possibility of generating these nanomaterials by a greener route has added an impetus to transforming farming practices. When these agents are produced using eco-friendly and green methods, they would help the agricultural community avoid harmful chemicals and thereby help evolve a healthy environment.

5.1. Fertilizers. The primary function of fertilizers is to maintain a balance in the mineral content to raise the yield. The excessive use of these mineral fertilizers may cause serious problems for soil fertility. Nanofertilizer formulations synthesised by green methods are found to supply a balanced supply of essential minerals with minimum intervention and also impart pest protection efficiency. Various categories of nanomaterials widely used to design fertilizers, as depicted in Figure 2, are recently reviewed by Guo et al. [35] with a comprehensive evaluation of their importance and limitation in agricultural practices.

Among the various important metals, zinc is one of the main micronutrients widely studied as leaching of Zn is posing a serious threat to crop yield since the past two decades. ZnO nanoparticles [36] at three different concentrations of 40, 80, and 120 ppm on wheat farms in the harvest stage have benefited the height of the plant and the weight of the seed, which was much higher than that obtained using traditional chemical zinc in the form of zinc nitrate. Alternatively, such physiological and morphological changes can also be affected by copper oxide loaded onto chitosan/alginate nanoparticles [37]. This leads to a spherically shaped 300 nm shell which encapsulates CuO and slowly releases Cu which is very essential for seedling growth. The polymeric-like shell has good adhesive properties and hence forms a protective layer against the loss of nutrients, preventing premature degradation. The germination evaluation results on *Fortunella margarita Swingle* seeds showed a clear synergic effect on epigean and hypogean parts. The Zn and Cu [38] nanoparticles in combination effectively influenced the morphological parameters that intensely affected the biochemical traits of the basil plant and exerted antioxidant activity. The nanoparticles of Zn and Cu which originated from the basil extract are said to be formed by reducing agents such as vitamin C, sucrose, flavonoids, or oxalic acid. The study promotes the quantity and quality of basil with the dual benefit of reducing fertilizer consumption and toxicity.

While plants are constantly challenged by fluctuating environmental metal ion concentrations and researchers worldwide are striving to strike upon the right proportion of the N-P-K ratio, the quantities of some major metals such as Ca, Mg, and S are highly crucial. A promising strategy for optimal nutrient management has recently been reported through K- and N-doped amorphous calcium phosphate [39]. Nitrogen incorporated through urea and nitrate by modulating reaction conditions facilitates a slow release owing to the two different chemical forms. The chemical state of the metal plays a vital role as it decides the absorption kinetics that determines the ease with which the roots absorb it. Therefore, a suitable platform that can supply the metal in an appropriate oxidation state becomes highly important. The nano-sized surface layers of zeolites have the property of slowly releasing metals which are used to deliver Fe^{3+} ions through the zeolite/Fe_2O_3 nanocomposite [40], which has potential for commercialization. A slow consistent release of Fe nanoparticles was confirmed, though the specific efficiency towards various crops needs to be determined.

5.2. Nanopesticides. The use of nanopesticides synthesised by a green route is a well-recognised area. Pesticides in the nano form are becoming a prominent part of agriculture due to their ability to solve many problems pertaining to pesticide toxicity. Nanopesticides can contain either the effective ingredient in nanosize or the ingredient being doped with

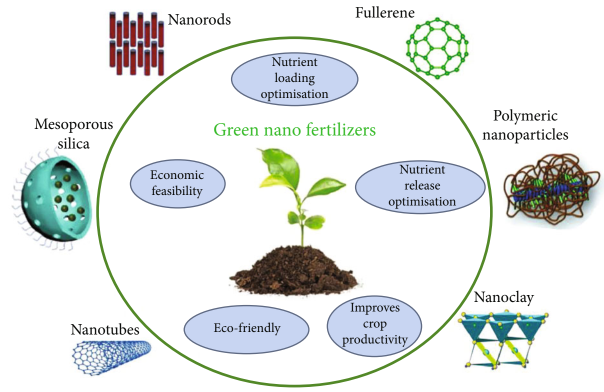

Figure 2: Different types of nanostructured materials in practical agricultural practice.

the nanomaterial, which improves the dispersibility, biological compatibility, performance, shelf life, functionality, and agricultural cost of pesticides and hence is considered to be a better alternative to the traditional pesticides. Nisha Raj et al. [41] have recently reviewed and elaborated on the various aspects of nanoagrochemicals such as nanoencapsulation, methodologies involved in the synthesis, enhancement of productivity in agriculture, influence on horticulture, and contribution to crop conservation. One of the promising applications of this technology is the regulated and controlled release of pesticide chemicals which greatly reduce waste pollution.

Graphene oxide is intelligently used as a nanocarrier for revolutionizing the application of pyrethroid pesticide [42] against spider mite which is a phytophagous mite pest. The newly designed GO–pesticide nanocomposite is found to exhibit a good loading capacity and has an excellent release behaviour both indoor and field. A uniform dispersion and effective adsorption on the cuticle of spider mites and bean plant leaves demonstrate its efficiency and prospects for practical applications.

Similar satisfactory results are also observed against microbial pests *Acidovorax oryzae* along with *Rhizoctonia solani* [43] for enhanced rice production by chitosan-magnesium nanocomposite and a simple chitosan nanocomposite against *Spodoptera litura* [44] in the larval phase. The former nanocombination, a native Bacillus sp. strain RNT3, was utilized to prepare spherically shaped nanocomposite in the range 29 to 60 nm which could destroy the cellular organelles of the pathogen. Such biologically synthesised nanocomposites not only contribute significantly to pest management but also can serve as a platform for degradation and removal of pests after the intended use. An example of this kind of phenomenon is reported on degrading acephate pesticide using MCM-41/Co_3O_4 nanocomposite [45] prepared from rice husk silica gel and peach leaves. The composite generates intermediates that are susceptible to visible light and highly sensitive to photocatalytic activity. Apart from these, synthesis of silver nanocomposites [46] using the extracts of bioactive red seaweeds has proved to possess nanopesticidal potential. Synthesis involves reduction of Ag^+ to Ag^0 using red seaweeds *G.*

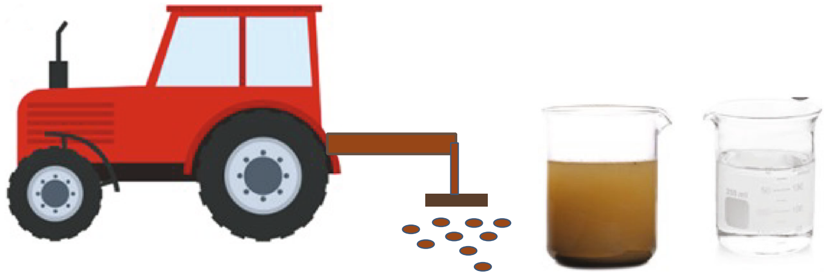

Figure 3: (a) Model diagram of magnetic collection of nanoparticles from soil; pH-responsively controlled-release pesticide suspension [48].

corticata, *G. edulis*, *H. musciformis*, and *S. hypnoides* indicated by a clear change in color across 410 nm and 430 nm. One of the prominent contributions to the green nanopesticides is the synthesis of ZrO nanoparticles against twig blight disease caused by the most deadly fungal pathogen of the past decade *Pestalotiopsis versicolor* [47] in bayberry plant. Optimal activity of the nanooxide at 20 μg mL^{-1} was observed in inhibiting twig blight on the leaf of these plants. A remarkable innovation in this area is the development of pesticide-loaded magnetic nanocarriers such as high porosity diatomite/Fe_3O_4 and subsequent coating with chitosan, which enables pH-responsive regulated release pesticide [48] that can be collected by application of an external magnetic field as indicated in Figure 3. This technique offers a high collection ratio without harming the soil quality whose efficiency can be measured by a magnetometer. These pesticide release systems attempt to reinforce the efficacy, impact, and sustainability of nanotechnology as a substitute for toxic chemicals in agriculture.

5.3. Soil Quality and Water Retention. The depletion of soil fertility on farmlands across the world is an issue that must be addressed with serious attention to meet the needs of the growing world population and social changes. In this regard, nanotechnology, through its unique material properties, has the potential to improve soil quality or mitigate nutrient imbalance by providing or carrying macro- and micronutrients. The large surface area, high adsorption capacity, and porous surface enable them to be controlled by release and act as efficient vehicles by encapsulation to carry the nutrients.

One of the serious concerns is the cadmium uptake by plants triggered by the large content of Cd^{2+} salts. Several cases have been reported in which the large specific surface area of nanomaterials helps in determining the uptake of cadmium [49]. The effect exerted on the nutritional quality includes absorption where Cd (II) is converted into an exchangeable form that can be assimilated by the seedlings or by a chemical transformation that increases the tolerance to cadmium ions by a regulated metabolic pathway. A study through an electrokinetic model [50] reveals Cd migration that shows a high Cd^{2+} adsorption efficiency up to 434.78 mg/g beyond pH 4. In addition, other metals such as bivalent lead and copper [51] along with monovalent potassium and sodium showed an active response. Such nanoremediation is also observed to reduce soil toxicity towards other metal pollutants [52] using graphene oxide validated by the Spanish official methodology, and few similar examples are listed in Table 2.

The techniques discussed so far can also be extended to soils contaminated with more than one metal ion. Hybrid bionanocomposites incorporating filamentous fungi [61] have been popularly used recently in the immobilization of Cd and Pb with Aspergillus niger found to be more efficient than Penicillium chrysogenum. Both heavy metals were found to be independently one to four times that of nanohydroxyapatites.

Moreover, the uptake of metals is closely related to moisture in the soil [62], and hence, the moisture content is considered to be a crucial parameter in most irrigational regimes [63]. The integration of nanomaterials into conventional agricultural practices can improve water-absorbing and retention properties. A huge stride in this direction is the development of low-cost superabsorbent nanocomposite that can be used to encapsulate conventional fertilizers [64] so that slow release is ensured as recommended by the Committee for European Normalization. A consistent release under varying pH and different concentrations of saline solutions proves its agricultural applications and water retention capability. A similar functionality is exhibited by xanthan gum-cl-poly (acrylic acid)/AgNPs hydrogel nanocomposite [65]. The embedded nanosilver particles which are characterised by several analytical techniques enable the composite towards water retention over sixty days. Also, it is observed that the composite releases KCl in a kinetically controlled manner with 5.458×10^{-6} m^2/h and 1.453×10^{-7} m^2/h being the initial and final rate of diffusion coefficient, respectively. These biopolymer-based hydrogel composites have a dual advantage of soil conditioning and biodegradability. The novel application of this technology is reflected in the development of carboxymethylcellulose along with hydroxyethylcellulose bridged with citric acid [66] and galactomannan fenugreek cross-linked by borax [67] where the water retention time can be extended up to 2 to 11.5 days at a temperature of 20°C with 60% humidity. The soil mixed with the galactomannan-borax fenugreek galactomannan-borax (FGB) increased the swelling index of sandy soil which is an indication of the increase in the water retention time as shown in Figure 4.

Despite the excellent efficiency exhibited by these water holding materials, unification with clay composites and

Table 2: Examples of soil remediation using nano-based material.

Nanomaterial	Dosage of nanomaterial	Contaminant in soil	Ref
Polyvinylpyrrolidone stabilized nano-zero-valent iron	0.01 g	Trichloroethylene	[53]
Nano-Fe/Cu	10 g per layer	Nitrate ions	[54]
Multiwalled carbon nanotubes	1, 2.5, 5 wt%	Cr(VI)	[55]
Modified carbon black nanoparticle	1% *w/w*	Petroleum	[56]
Single-walled carbon nanotubes	0.058, 0.145, 0.29 wt%	DDT	[57]
Goethite nanospheres	0.5, 2, 5, 10 wt%	As	[58]
Nano-Fe_3O_4@C-COOH	0.6, 1.3, 2.0, 2.6, 3.3, 4.0 wt%	Pb	[59]
Magnetite nanoparticles	1% *w/w*	As	[60]

machine installations would intensify water retention through adoption of green nanomaterials.

5.4. Nanosensors. Biological entities have eased the understanding of nanoparticle-biomolecule interactions by inducing positive responses in soils and plants. As conventional sensors adopt tissue-destructive techniques and pose limitations on precise measurements, most sensing systems pertaining to agriculture now resort to green nanosensors that can efficiently translate chemical reactions into quantified voltages. Often, these nanosensors apart from holding sensitive signalling molecules on their surface also possess antimicrobial [68, 69] and antifungal [70] action.

Various novel receptors are designed to detect traces of heavy elements such as Hg^{2+}, Pb^{2+}, and Cr^{6+} that recirculate in the food chain causing degenerative toxicity. Chitosan, a naturally available polycationic linear long-duration polysaccharide originating from chitin, is interestingly widely used in the area of nanosensors. The first-ever chitosan capped gold nanoparticles act as a Hg (II) sensor [71] when tested on agricultural soil which works on plug and play mode and is found to be compliant with the "gold standard." Similarly, ryegrass, which aids the one-step synthesis of carbon dots [72], was found to be useful for chelating heavy metals. Regarding chitosan-based nanocomposites, its association with the surface plasmon resonance phenomenon makes it popular in building a detector for glyphosate [73] and is considered a prominent herbicide highly polar and water-soluble. Chitosan is composited with zinc oxide or graphene oxide and coated onto the Au chip using the spin coating technique as represented in Figure 5.

The sensor is widely used as a thin film probe for the on-field detection of glyphosate in natural soil and waters. The technique used resembles another sensor for glyphosate made of a chitosan composite [74] with reduced graphene oxide and carbon nanotubes with a double wall along with Fe_3O_4 with an octahedral configuration. The composite is screen printed on gold electrodes forming an electroactive surface area 1.7 times larger than the bare electrode. The method analysed for river water samples utilised for agriculture holds a great promise as an efficient sensing platform.

The report has inspired another chitosan composite with carbon nanofiber with nanocopper as the supporting matrix used to fabricate an electrochemical sensor for carbendazim [75], which is of great environmental interest. The biocompatible chitosan functionalized platform of Cu-containing carbon nanofiber has a high degree of selectivity, a low detection limit, and a wide range of sensitivity 0.8–277.0 μM. The detection process is validated using real soil-washed water samples from farmlands using linear sweep voltammetry.

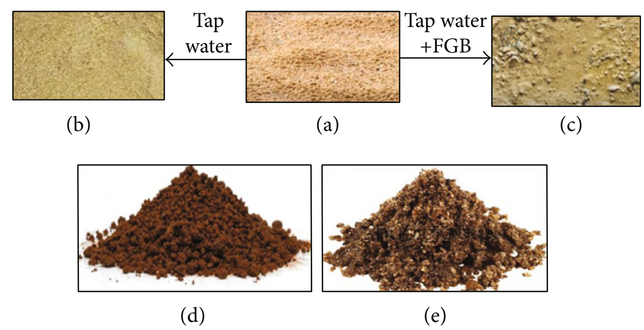

Figure 4: (a) Saturation of sandy soil with tap water; (b) sandy soil; (c) saturation of sandy soil with tap water along with fenugreek galactomannan-borax hydrogel; (d) untreated sandy soil with low porosity; (e) fenugreek galactomannan-borax hydrogel-treated sandy soil with enhanced porosity [67].

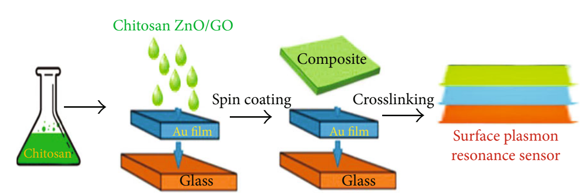

Figure 5: Scheme for the fabrication of surface plasmon resonance sensor.

Several natural polymeric compounds are being explored as a nanocompound sensing platform because they are biodegradable and readily eliminated. Lignin, which is a widely found phenolic polymer, is used to stabilize silver nanoparticles which possess colorimetric sensing properties [76], with respect to arsenic, iron, and lead in nanomolar concentrations. A solution of 100 to 10 mM showed a red shift, and a solution of 1 μM to 1 nM showed a blue shift due to metal reduction by nanosilver particles. Colorimetric

Table 3: Comparison of analytical methods of green nano-based sensors in agriculture.

Nanomaterial in sensor	Sensing methodology	Sensing target	Limit of detection	Ref
Thiol–gold	Colorimetric	Listeria monocytogenes	0.015 and 0.013 ng mL^{-1}	[79]
Fluorescent–SiO_2	Fluorescence	Brucella spp	50 μL	[80]
Bis-aniline–cross-linked Au	Surface plasmon resonance	Neomycin	2.00 ± 0.21 pM	[81]
Hyperbranched polyethyleneimine scaffolds–AgNPs	Fluorescence quenching	Nitrite	100 nM	[82]
FDH–single-walled carbon nanotube paste electrode	Electrochemical detection	D-Fructose	1 μM	[83]
DLS–superparamagnetic beads–AuNPs	Dynamic light scattering	Aflatoxin	37.7 ng L^{-1}	[84]
AuNPs	Immunodipstick	Vitamin B12	1 mg mL^{-1}	[85]
MIP/sol–gel/MWNTs–CS/GCE	Electrochemical detection	Quinoxaline-2-carboxylic acid	4.4×10^{-7} mol L^{-1}	[86]
OVA–hapten conjugate and AuNPs	Lateral flow immunoassay	Sulfathiazole	15 ng g^{-1}	[87]
XOD/CHIT/Fe-NPs@Au/PGE	Electrochemical detection	Xanthine	0.1 μM	[88]

detection is extended to detect a broad-spectrum pesticide (O,O-diethyl-O-α-oximinophenyl cyanophosphorothioate) [77]. The contribution of this sensor is remarkable as the pesticide is popularly sold under the name "Phoxim" whose residues are posing a threat to human health. The authors used Lycii Fructus, a berry fruit, as a precursor to synthesise the carbon dots functionalized with amino, hydroxyl, and carboxyl groups that can hold silver nanoparticles. The nanosilver particles synthesised indicate the presence of pesticides by aggregation, which displays a color change from yellow to red. The silver particles for colorimetric aggregation properties are used not only to detect pesticides but also for pharmaceutical antibiotics used in treating infections. An excellent successful exploration is to incorporate silver nanoparticles conjugated to green synthesised gentamicin [78]. The gentamicin sensor is a significant step in the prevention of gentamicin-resistant bacteriocoenosis as it shows high sensitivity in the range of 1–100 μM, along with detection and quantification in the range of 0.29 μM and 1 μM.

These new sensors, which are adding to the list of existing systems as listed in Table 3, require no sophisticated instruments and mark the beginning of a new age with naturally derived, environmentally friendly green nanomonitoring systems.

5.5. Limitations and Future Challenges. Although nanotechnology holds many promises in agricultural technology, these compounds, being extremely small and highly soluble and possessing high reactivity because of their large surface area, may also have long-term effects leading to combined toxicity. Additionally, these compounds may trigger altered gene expression leading to nanogenetic manipulation with a severe change in color, growth, reduced pollen, and yield. Treating the root tips of *Allium cepa* with nanooxides is reported to cause cellular deformation through chromosomal aberration. Among simple oxides such as Al_2O_3, TiO_2, and ZnO, abnormal anaphase accompanied by sticky metaphase was exhibited by TiO_2 [89] in the concentration range 0.1, 10, and 100 mg/L. The severity of aberration is found to be maximum for TiO_2 and fairly lower in the case of Al_2O_3 and ZnO.

A similar comparative study between CuO-NPs and Al_2O_3-NPs of 18 nm along with 21 nm, respectively, is exploring the extent of the internalization and translocation in tomato plants [90]. The binding studies with TmDNA by fluorescence quenching revealed a higher activity of CuO nanoparticles compared to Al_2O_3 nanoparticles.

There is also a possibility of these nanocompounds entering the food chain. Some studies such as on soyabean [91] where chemical damage is caused, rice suspension cells [92] treated with multiwalled carbon nanotubes initiating a self-defence response, and magnetic nanoparticles causing brown spots on leaves of maize plantlets [93] due to genetic deformation [94] also predict the interaction of nanocompounds with plants leading to an imbalance in the uptake of nutrients. The study of in vitro oxidative damage caused by Ni nanoparticles, which triggers an antioxidant response, affecting the growth of Lycium *barbarum L* [95], has been shown to be highly damaging compared to its bulk counterpart $NiSO_4$.

These studies highlight the need for a deeper understanding of the vascular system of the plant with guided administration to the targeted sites. The site-specific nanotransfer potential could help to optimize the physiological and biochemical usage of these compounds to maintain a balance in plant hormones and nucleic acids in the localized areas of plant tissues. The effect of nanoparticles on biological pathways and the associated mechanistic factors hence deserve a risk assessment procedure at the genomic or biochemical level.

6. Conclusions

The application of nanotechnology at the global level has made many agricultural procedures faster, cheaper, and more accurate. Green nanotechnology with its eco-friendly means of generating functionalized nanoparticles has a great potential to dispense pesticides and fertilizers in a controlled manner, thereby avoiding collateral damage. This area of research has many novel solutions to offer in the area of plant growth of development and could also permit rapid advances in agricultural reproductive science. However, effective commercialization of green nanotechnology still requires a thorough understanding of these moieties with biotic or abiotic components and the possibility of bioaccumulation. The problems associated with safety issues, public perception, scalability, and regulating processing costs are the recognised future challenges in bringing green nanotechnology from R&D laboratories to industrial production. It is high time for the governments and nongovernmental organisations across the world to come together to form common regulations and norms to strictly monitor the commercialization and bulk usage of green nanocompounds in the agricultural sector.

Data Availability

All relevant data are included within the article.

Conflicts of Interest

All authors declare that there is no conflict of interest.

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