DOI: 10.54083/PHA/1.3.2023/96-101

Plant Health Arch., 2023, 1(3):96-101

Plant Health Archives

e-ISSN: 2583-9659
October-December, 2023

Article ID: PHA022

Review Article

Botanicals as a Source of Nanomaterial for Pest and Disease Management

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Conflict of interests: The author has declared that no conflict of interest exists.

How to cite this article?

Sharma *et al*., 2023. Botanicals as a Source of Nanomaterial for Pest and Disease Management. *Plant Health Archives* 1(3), 96-101. DOI: 10.54083/PHA/1.3.2023/96-101.

Abstract

Sustainable food production for a rapidly growing human population is one of the major challenges faced by the agriculture sector globally. Plant pests and pathogens cause significant reductions in crop production, with estimated global losses of 20-40% year^{-1}, resulting in an increased use of environmentally toxic pesticides & fertilizers. The growing numbers of studies in nanotechnology are producing novel applications in many fields of science, especially in plant biotechnology and agriculture. Nanomaterials (NMs) have been used in breakdown of pollutants and reported worldwide for several different environmental applications. They play an important role in agriculture as nano-fertilizers and nano-pesticides, prepared by many methods such as physical, green synthesis or chemical synthesis methods. Green synthesis involves use of biological resources as microorganisms or plant extracts and doesn't permit the use of any toxic chemicals, hence less bio-hazardous. Rate of reduction of metal ions using phytosynthesis has been observed to be much faster than microbial synthesis. Thus, it is considered as an accessible alternative for large scale production of nanomaterials, without use of chemicals. Phytosynthesized nanomaterials show excellent antibacterial effects, antifungal effects and anti-pest activity. *Ocimum sanctum*, *Azadiracta indica*, *Paederia foetida*, *etc*. had been successfully reported to be used in synthesis of many NMs of silver, gold, zinc, *etc*. Botanical nanomaterials offer considerable potential for increasing agricultural productivity and protection while reducing negative impacts on the environment and human health simultaneously.

Keywords: Green synthesis, Nanomaterials, Nanotechnology, Phytosynthesis

Introduction

Every year, agricultural production witnesses 20-40% losses due to insect-pests and diseases. To combat these losses huge numbers of chemical pesticides are predominantly used which are extremely toxic and non-environment friendly. Numerous innovative technological approaches to enhance environmental protection have emerged in recent decades (Villaseñor-Basulto *et al.*, 2019). As the demand for sustainability grows, evaluation of technological solutions is carried out not only for cost-effectiveness but also involves evaluating their capacity to either prevent the release of pollutants into the environment or remove pollutants from it, all while avoiding the creation of toxic by-products (Villaseñor-Basulto *et al.*, 2019). Ideally, these solutions should leverage renewable sources as well. Among the various technological advancements, the 21st century has seen a remarkable surge in the field of nanotechnology, emerging as a distinct branch of science renowned for its diverse applications and remarkable effectiveness (Smitha *et al.*, 2020). The development of nanodevices and nanomaterials has ushered in innovative possibilities in the realms of agriculture and plant biotechnology. In general, nanoparticles are defined as solid colloidal particles, containing both nano capsules as well as nanospheres (Souza *et al.*, 2019). As reported by many researchers, nanomaterials show promising activity as vectors due to their capacity to release drugs in an efficient and steady way. As of now, a range of toxic chemicals such as PEG, PAA and CTAB

Article History

RECEIVED on 11th July 2023 RECEIVED in revised form 16th October 2023 ACCEPTED in final form 23rd October 2023

are being employed either as reducing agents or stabilizing agents in the synthesis of nanomaterials.

History of Nanomaterials

Even though nanomaterials are product of modern technology, however the history of these nanomaterials (NMs) dates back to several thousands of years ago. About 1000 years ago, our ancestors used gold (Au) nanoparticles of different sizes used to produce different colours in stained glass windows. Later, in the modern era, in the year 1959, Richard Feynman in his lecture "There's plenty of room at the bottom", discussed about the scope of nano sized particles, after which he was recognized as father of Nanotechnology. After almost 15 years, Norio Taniguchi in 1974, coined the term "Nanotechnology". Several great discovers and inventions were made in the later period which boosted the field of nanoscience including the invention of the scanning tunneling microscope in 1981 and the discovery of fullerene in 1985. Later, in the year 2000, "National Nanotechnology Initiative" was launched in the United States. Two prominent workers in the field of nanotechnology from India Dr. Kattesh V. Katti, "Father of Green Nanotechnology" and Prof. C.N.R. Rao have made great developments in this area.

Nanomaterials - Method of Synthesis

Several methods are employed for the synthesis of nanomaterials. In the synthesis process, two main approaches are commonly standardized, *viz*., top-down approach and bottom-up approach. Top-down approach comprises of disintegration of bulk material to form nanomaterials such as in Sol-Gel, Lithography, Milling, *etc*. Bottom-up approach comprises of assembling or fusing small sized particles to form nanosized materials. Examples include- plasma etching, chemical vapour deposition, *etc*.

The nanomaterial synthesis is carried out either by physical, chemical or biological method. Physical methods of synthesis of nanomaterials includes processes like Plasma method, Microwave irradiation, High energy ball milling, Pulse vapour deposition, Electro spraying, Melt mixing, *etc*. On the other-hand, chemical methods of synthesis include use of chemical compounds in the formation process. To name a few, these are: Sol-Gel synthesis, Hydrothermal synthesis, Polyol synthesis, Microemulsion technique, *etc*.

Of all the synthesis methods, biological synthesis is currently in spotlight as the most preferred, safest and environment friendly method. The conventional physical and chemical processes employed for nanomaterial production come with significant drawbacks, including the formation of defective surfaces, low production rates, elevated costs and substantial energy demands (Villaseñor-Basulto *et al.*, 2019). Chemical synthesis procedures frequently entail the utilization of harmful substances, the production of perilous secondary products, and the possible dispersion of precursor chemicals into the surrounding environment (Villaseñor-Basulto *et al.*, 2019). It is crucial to explore greener strategies for producing nanomaterials that are environmentally friendly, non-toxic and minimize the ecological footprint of treatment procedures to the greatest extent feasible. Employing eco-friendly green processes for nanomaterial synthesis offers several noteworthy advantages in comparison to the commonly used chemical processes (Husen and Siddiqi, 2014; Dutta *et al*., 2015). For instance, traditional chemical processes like pyrolysis and attrition often yield ZVI-NPs with notable drawbacks, including the formation of defective surfaces, low production rates, substantial costs, and high energy demands (Herlekar *et al.*, 2014). Biological synthesis processes entail the blending of specific quantities of metal ions with plant extracts or microorganisms under suitable conditions (Husen and Siddiqi, 2014; El Shafey, 2020). These methods serve as eco-friendly alternatives to traditional synthesis techniques, with the primary goal of diminishing the use or generation of toxic elements inherent to conventional approaches. They originate from sustainable sources, and notably, biosynthesis has the potential to significantly decrease production costs in a practical and scalable manner.

The adoption of biological synthesis protocols for nanomaterial production has seen a notable uptick in recent years. These protocols offer several advantages, including (i) the implementation of environmentally friendly methods that eliminate the use of toxic chemicals, (ii) cost-effectiveness by avoiding high-pressure and high-energy requirements, and (iii) the capability to generate small-sized nanoparticles (Villasenor-Basulto *et al*., 2019; Pandey and Jain, 2020). A diverse range of biological resources has been harnessed in the past for nanoparticle synthesis, encompassing microorganisms (such as fungi, yeasts, algae, viruses and bacteria) as well as various components from plants (like fruits, peels, seeds, leaves, roots and flowers).

The plant-mediated biosynthesis of nanoparticles has emerged as a significant highlight, driven by the increasing demand for environmentally friendly technology development (Akhter *et al.*, 2016; El Shafey, 2020). The active biological component itself serves as both a capping and reducing agent, thereby reducing the overall cost of the synthesis process and promoting sustainable production (Li *et al.*, 2011). Plant extracts offer exceptional cost-effectiveness for nanoparticle generation due to their distinctive characteristics. Recent reports indicate that numerous herbs and plant constituents contain elevated levels of antioxidant compounds, such as polyphenols, sugars and amino acids, which can be effectively employed as both reducing and capping agents for nanomaterials (Bhuyan *et al.*, 2017; Villaseñor-Basulto *et al.*, 2019). Their utilization in nanomaterial synthesis is well-suited for upscaling processes and producing stabilized products. Various plants with wide range of plant parts are used to synthesize different NMs. The reason behind is that they increase the rate of synthesis & enhances the monodispersity of nanomaterials. Furthermore, the reduction rate of metal ions using plant extracts has been observed to be significantly faster compared to that achieved with microorganisms (Rauf *et al.*, 2019), and additionally, using microorganisms for such processes can present biohazard concerns. Thus, plant synthesis or phytosynthesis is regarded as an accessible alternative for large-scale nanomaterial production.

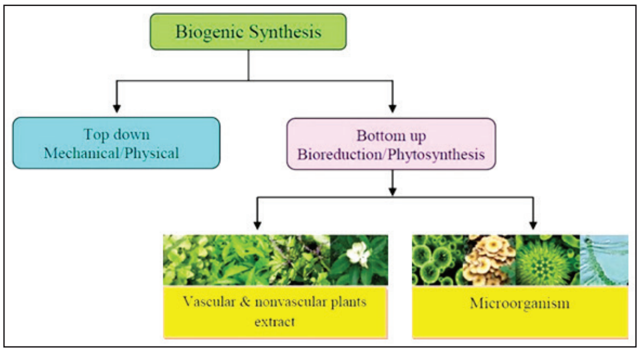

Figure 1: Flow diagram for biogenic nanomaterial synthesis (Husen and Siddiqi, 2014)

General Methodology of Phytosynthesis

Phytosynthesis, *i.e.*, synthesis from plants is an exceptionally swift, straightforward and cost-effective process that gets completed within minutes. Numerous unique and readily available indigenous plants (Table 1) have been employed for quick plant mediated control of pests and diseases. Unfortunately, these methods are often neither documented nor adequately developed due to the fact that the knowledge is typically transmitted through oral traditions from one generation to the next (Husen and Siddiqi, 2014). Leveraging appropriate scientific research to assess the invaluable botanical resources could lead to significant advancements in nanoparticle synthesis, with applications spanning the fields of healthcare, cosmetics, disease management for both plants and animals, and environmental remediation (Husen and Siddiqi, 2014; Worrall *et al.*, 2018). The synthesis of nanomaterials using plant extracts holds immense potential for the forthcoming decades. However, there is still a requirement for a commercially viable, economically feasible and environmentally friendly route to explore the ability of natural reducing constituents to produce nanomaterials. This aspect remains relatively unexplored in scientific research. The use of phytochemicals in nanoparticle synthesis holds the promise of diminishing cytotoxicity, genotoxicity and immunotoxicity due to their antioxidant characteristics, thereby augmenting biocompatibility (Villaseñor-Basulto *et al.*, 2019). Plant extracts abundant in flavonoids and polyphenols have been effectively employed in the eco-friendly synthesis of various nanoparticles, including Ag, Au, Cu, ZnO and others.

The general protocol for phytosynthesis of nanoparticles is as follows:

• Initially, fresh plant components are gathered and thoroughly rinsed with distilled water to eliminate dust particles. Subsequently, they are sun-dried to remove any remaining moisture (Gogate *et al.*, 2018).

• Then, the leaves are cut finely and added in glass beaker along with sterile distilled water, and boiled for 5-10 minutes until the color of the aqueous solution undergoes a noticeable change (Gogate *et al.*, 2018).

Table 1: Plants used for synthesis of nanomaterials

Plants	Metal/ Metal oxide nanoparticles	NM Application
Arachis hypogaea (Groundnut)	Silver (Ag)	Antifungal
Quisqualis indica (Red Jasmine)	Silver (Ag)	Pest management
Simarouba glauca (Paradise tree)	Silver (Ag)	Antibacterial
Styrax benzoin (Sambrani)	Silver (Ag)	Antibacterial
Tecomella undulata (Rohida)	Silver (Ag)	Antimicrobial
Zornia diphylla (Palash)	Silver (Ag)	Pest management
Cucurbita pepo (Pumpkin)	Gold (Au)	Antimicrobial
Curcuma longa (Turmeric)	Gold (Au)	Antimicrobial
Cymbopogon citratus (Lemon grass)	Gold (Au)	Antibacterial
Cymbopogon citratus (Lemon grass)	Gold (Au)	Pest management
Pistia stratiotes (Water lettuce)	Gold (Au)	Antibacterial
Tagetes sp. (Marigold)	Copper (Cu)	Larvicidal
Pongamia pinnata (Karangi)	Zinc oxide (ZnO)	Antimicrobial
Moringa oleifera (Drumstick)	Cerium oxide (CsO)	Antibacterial
Vitis vinifera (Grapevine)	Ag-Fe_3O_4	Antibacterial
Allamanda cathartica (Allamanda)	Silver (Ag)	Antimicrobial
Helianthus sp. (Sunflower)	Copper (Cu)	Larvicidal
Catharanthus roseus (Periwinkle)	Copper (Cu)	Antimicrobial
Paederia foetida (Stink vine)	Silver/ Gold (Ag/ Au)	Antimicrobial
Ocimum sanctum (Holy Basil)	Silver (Ag)	Pest management
Rice husk	Ag-SiO_2	Antibacterial

(Source: Villaseñor-Basulto *et al.*, 2019)

• The aqueous extracts are subsequently cooled to room temperature and filtered using Whatman filter paper No. 1 before undergoing centrifugation to eliminate the denser biomaterials (Gogate *et al.*, 2018).

• Finally, the plant extract so formed is added separately into aqueous solution of metal solution & stirred magnetically at room temperature.

• After 1-2 days the resulting solution changes its colour, indicating the formation of nanoparticles (Dutta and Kaman, 2017).

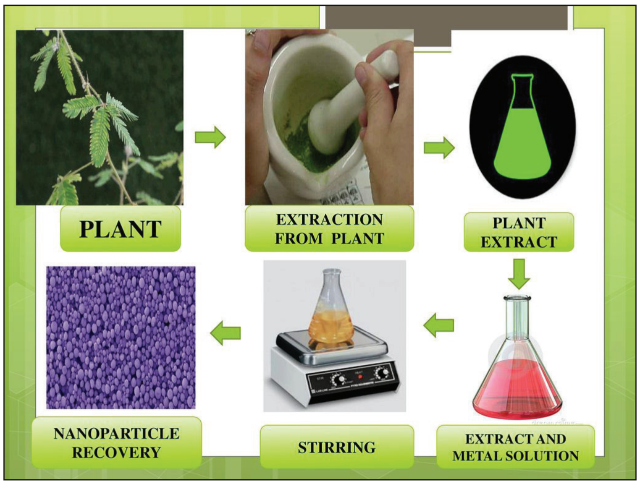

Figure 2: General steps for synthesis of metal nanomaterial (Murthy *et al.*, 2018)

Following the synthesis, the nanomaterials are characterized using various equipments based on their size, shape, crystallinity, functional groups, zeta potential, *etc.* These give the confirmation of the formation of the nanoparticle. A homogeneity in these properties is very important for their uniform application (Gogate *et al.*, 2018).

Wide numbers of equipments used for characterization are as follows:

1. UV-Vis spectroscopy
2. Dynamic light scattering
3. Transmission electron microscopy
4. Scanning electron microscopy
5. Zeta potential/ sizer, *etc.*

Factors and Mechanism of Nanomaterial Synthesis

The nanomaterial synthesis process is controlled by a number of factors acting directly or indirectly during the reaction process. The nature and concentration of the plant extract containing some active biomolecules, along with the salt concentration, prevailing pH, incubation temperature, contact time and the presence of phytochemicals such as terpenoids, flavonoids, proteins and phenolic compounds, collectively govern and influence the entire process of nanomaterial synthesis (de Oliveira *et al.*, 2014). Even a slight change in pH can result in change of charge in the phytochemical compounds in the extract, resulting in altering their capacity to bind with and reduce the metal play a pivotal role in the process of metal ion reduction (El Shafey, 2020).

The synthesis mechanism unfolds in three distinct phases: the activation phase, the growth phase and the termination phase. In the initial activation phase, the reduction of metal ions occurs and nucleation of atoms takes place. During the growth phase, smaller adjacent nanoparticles coalesce to form large size particles & following by increased thermodynamic stability of the nanomaterials. The termination phase is the final phase of synthesis, during which stabilization of particles occurs. The stabilization process depends on the plant extract (Love *et al.*, 2015).

Challenges

The presence of specific compounds, such as oils, can influence the quality and result in varied shapes of nanomaterials. The primary challenge lies in identifying the chemical compounds responsible for nanoparticle reduction and stability to enable efficient nanomaterial production

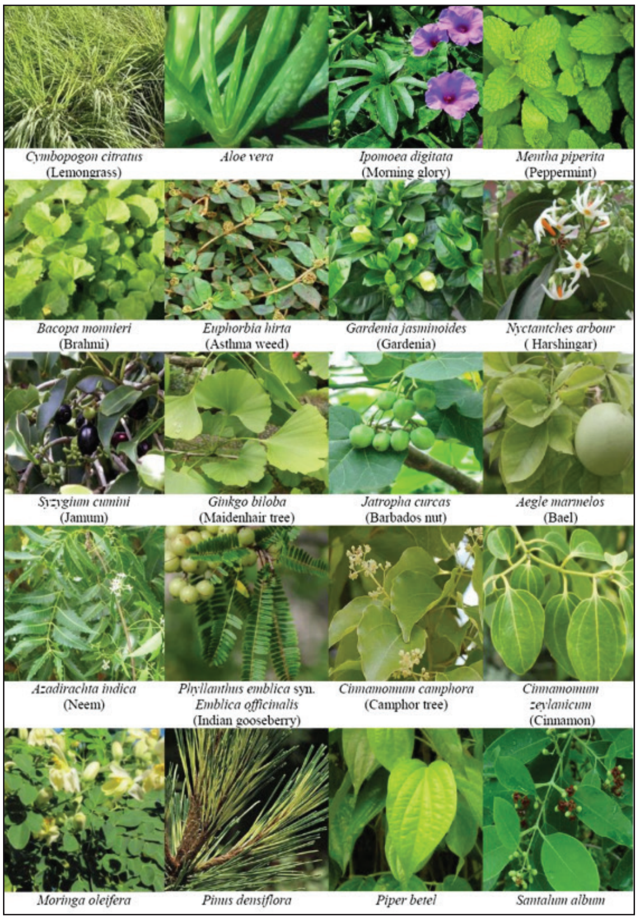

Figure 3: Plants used in nanomaterial synthesis (Husen and Siddiqi, 2014)

cations and anions during the synthesis process. The resultant nanomaterial may have different size, shape and yield. Proteins and carbohydrates are among the crucial constituents of plant extracts, serving as essential reducing agents responsible for the formation of nanomaterials and the reduction of metal ions (El Shafey, 2020). The functional amino groups and proteins found in these plant extracts

(Villaseñor-Basulto *et al.*, 2019). The chemical composition of plant extracts and the choice of suitable plants are contingent upon factors like geographical location, growth patterns, and plant utilization, which can impact the availability of plant materials for scaling up nanomaterial production. Moreover, a lack of comprehensive investigations into the mechanisms of nanoparticle production and the potential effects of various reaction parameters on the final product exist. Additionally, the characterization of nanomaterials synthesized using plant extracts remains challenging, as relatively few dedicated studies have been conducted to systematically analyze these materials.

Future Line of Work

Over 200 companies are actively engaged in research and development in the field of applying nanotechnology across a wide range of industries. In particular, approximately 150 applications of nanotechnology in the food sector are currently in various stages of development, with more than 500 patents in the pipeline for these innovations (Husen and Siddiqi, 2014). The global market value of nanomaterials is projected to reach an estimated 98 billion USD by the year 2025 (Jeyaraj *et al.*, 2019). The development of nanoformulations and their myriad applications make plant-based nanomaterial preparation a promising and favorable area for various studies (El Shafey, 2020), owing to the advantages it offers over conventional synthesis methods. Development in the area of phytonanotechnology will promote the idea of precision farming and permit judicial use of natural resources in place of toxic chemicals causing environmental hazards.

Conclusion

The production of nanomaterials utilizing botanical extracts represents an emerging frontier in nanotechnology, offering a superior alternative to chemical synthesis. These innovative biogenic methods are genuinely eco-friendly, aligning with sustainable practices (Smitha *et al.*, 2020). Nanomaterials synthesized through phyto-methods exhibit remarkable antibacterial, antifungal and anti-parasitic properties (Zhang *et al*., 2015). These nanomaterials serve as alternatives to traditional pesticides in the control and management of plant diseases while also acting as efficient fertilizers. There is a growing need for intensified research efforts to tap into unexplored bioresources and unlock the tremendous potential of nanotechnology for the betterment of humanity, paving the way for new horizons of innovation.

Acknowledgement

The authors acknowledge the authority of CAU (Imphal) for the guidance, encouragement and support for writing the review article.

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