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Review

Gold and silver nanoparticles: Green synthesis, microbes, mechanism, factors, plant disease management and environmental risks



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ABSTRACT

Metal nanoparticles were being used in different processes of developmental sectors like agriculture, industry, medical and pharmaceuticals. Nano-biotechnology along with sustainable organic chemistry has immense potential to reproduce innovative and key components of the systems to support surrounding environment, human health, and industry sustainably. Different unconventional methods were being used in green chemistry to synthesize gold and silver nanoparticles from various microbes. So, we reviewed different biological processes for green synthesis of metal nanoparticles. We also studied the mechanism of the synthesis process and procedures to characterize them. Some metallic nanoparticles have shown their potential to act as antimicrobial agent against plant pathogens. Here, we outlined green nanoparticles synthesized from microbes and highlighted their role against plant disease management.

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1. Introduction

Nanobiotechnology has been advanced as a substitute to replace environmentally destructive technologies and productions because of their negative significances being faced globally and the insufficient timeline to gain beneficial results (Hurst, 2020). It is assumed that by the end of 2020 green chemistry may have an Economic payoff by saving up to USD 65.5 billion (Menges, 2017). The circular economies (waste and emissions control, the maintenance of goods and resources in use, and the recovery of natural resources) always required to have a balanced economic development, resource management and sustainability, and conservation of the environment (Chen et al., 2020). The challenge for developing countries which biodiversity-rich is using their biological resources in methods and production processes, which need to be done along with environmental sustainability using natural resources (Zuin et al., 2020). That's why different approaches have been adopted in this field by using modern green process engineering (MGPE), like the production of nanoparticles (NPs) from biological systems (Mondal et al., 2020) Nanoparticles (NPs) are a broad series of substances with measurements less than 100 nm, that can be utilized in different processes of different sectors, such as agriculture, materials and manufacturing, mechanical industries, medical, pharmaceutical, environmental due to their multiple characteristics (Guleria et al., 2020). The use of agricultural NPs is now being investigated in nano-barcoding, nano-sensors, seed germination, transport hormones in plants, transfer of target genes, water management and plant disease management (Hayles et al., 2017). Plant pathogens and pests' reason significant declines in production yield, with global decline projected at 20% – 40% each year (Flood, 2010). Recent pest management depends intensively on the use of chemicals, such as herbicides, fungicides, and insecticides. Although, use of aforesaid chemical have attractive benefits such as high availability, reliability, and rapid action, but toxic substances resulted in severe impacts to non-targeted objects, and pathogens are becoming more stronger and developing immunity against different pesticides, herbicides and fungicides (Ghormade et al., 2011). This phenomenon supported the idea of some incentive to improve cost-effective, high-performance fungicides with minor impacts to the environment. The utilization of biological systems, such as bacteria, fungi, and algae, to synthesize NPs has benefits such as lower energy usage and clean and safe technology without the use of harmful chemicals (Mie et al., 2014). Utilization of different nanotechnology techniques in protecting plants against different diseases is just at its initial phase (Elmer and White, 2018). NPs can protect the plant by adopting two procedures (a) NPs by themselves promoting crop protection or (b) NPs as serving carriers for existing an individual or combine pesticides or other active compounds (Worrall et al., 2018). Therefore, in current review, we have tried to observe complete aspect of the biosynthesis and mechanisms of metal nanoparticles from microbes like fungi, bacteria, and algae along with their ability to act as an antimicrobial agent and the mode of their action.

2. Green synthesis of nanoparticles

Day by day, multiple techniques are produced for the nanoparticle synthesis. Biological procedures, physical procedures, and chemical procedures are the three basic groups of these tech-

niques. Anyhow the most appropriate procedure to synthesize NP is the biological procedure owing to its uncomplicatedness, harmlessness, and cost-effectiveness. The reducing and capping agents are performing a significant role in the NP synthesis. Chemical materials that are employed in the physical and chemical procedures of synthesis of NP are hazardous and extremely toxic, which are responsible for environmental issues. Chemical and microorganisms being used in biological processes are not only harmless to surrounding environment but also safe for no targeted organisms. That's why most appropriate and recommended process for NS synthesis are biological processes (Awwad et al., 2013). At present there is dire need of developing sustainable procedures and methods to nanoparticles, as NPs are needed to use in areas are in direct link of humans (Shams et al., 2013). By developing understanding of green and sustainable technologies, we can develop safe strategies to use NPs and can be grouped in following five methods:

2.1. Polysaccharide method

Green synthesis of AgNPs using the polysaccharide method (cellulose) from biological applications as an example of biological applications for environmental sustainability. water hyacinth (biological applications) has a high percentage of cellulose in its shoot and roots. The cellulose was extracted from the shoot or roots of the plant and used as reducing and stabilizing agents. Also, the particle shape and size were under control by changing the pH of the solution and reaction time (Mochochoko et al., 2013).

2.2. Tollens method

The Tollens reaction is mild, facile, and managed in a single biosynthetic phase. In this method, Tollens-reagent and reducing sugars have based role in the Ag⁺ ions reduction, yielding AgNPs with a high degree of size- and shape-control of AgNPs. the smallest size of AgNPs has ranged from 5 to 8 nm when used triazole sugar (Korbekandi et al., 2013).

2.3. Irradiation method

The gamma irradiation method is fairly suitable to synthesis the small metallic NPs. This method can be carried out in absence of reducing agents at room temperature. The gamma irradiation utilized a templating model to confine the locus of reaction into virtual "nanoreactors" or "nanomolds," to controlled in particle size and shape or template-free model (Flores-Rojas et al., 2020).

2.4. Polyoxometalates method

Polyoxometalates (POMs) are a vast group of molecular metal-oxide have much application owing to their unique compositions, structures. Meanwhile, reduced forms of POMs have a great capacity of electron storage and/or transfer capacities, and therefore, it can be engaged to serve as an effective acceptors or donors of numerous electrons. Henceforth, soluble polyoxometalates are proficient in synthesizing noble NPs by multi-electron redox reactions by a one-step reaction at room temperature (Cauerhff and Castro 2013).

Table 1
AgNPs and AuNPs of varying size and shape from fungal species.

Fungi	Nanoparticles	Characterization		Location	Reference
		Size	Shape		
<i>Alternaria alternata</i>	Au	12–29	Spherical, triangular, hexagonal	Extracellular	Sarkar et al. 2012
<i>A. oryzae</i> var. <i>viridis</i>	Au	10–60	Spherical,	Mycelial surface	Binupriya et al., 2010
<i>Fusarium oxysporum</i>	Au	20–50	Spherical,	Extracellular	Husen and Siddiqi, 2014
<i>P. fellutanum</i>	Ag	5–25	Spherical	Extracellular	Kathiresan et al., 2009
<i>T. koningii</i>	Au	10–14	Spherical	Cell-free filtrate	Maliszewska 2013
<i>T. viride</i>	Ag	5–40	Spherical	Extracellular	Fayaz et al., 2010
Bacteria					
<i>Bacillus endophyticus</i>	Ag	5–35	Spherical	Intracellular	Gan et al., 2018
<i>Streptomyces griseoplanus</i>	Ag	19–40	Spherical	Extracellular	Vijayabharathi et al., 2018
<i>Nocardopsis flavascens</i>	Ag	5–50	Spherical	Extracellular	Ranjani et al., 2018
<i>Caldicellulosiruptor changbaiensis</i>	Au	20–60	Spherical	Extracellular	Bing et al., 2018
<i>Shewanella loihica</i>	Au	2–15	Spherical	Intracellular/Extracellular	Ahmed et al., 2018
<i>Micrococcus yunnanensis</i>	Au	15–55	Spherical	Extracellular	Jafari et al., 2018

2.5. Biological method

It has been shown that biological synthesis is significant nanofactories that hold enormous potential as eco-friendly and profitable equipment, evading noxious, severe substances, and the great energy needs essential for chemical and physical procedures. The biological protocol includes the synthesis of NPs by utilizing organism like plant and microorganisms such as bacteria, fungi, and yeast. The theory of biological synthesis based on many organisms were become evolved to tolerate conditions of enriched metal concentrations. Such micro-organisms have ability to change the more toxic chemicals and substances in less toxic and harmful components or convert them in complete nontoxic substances (Sharma and Bisen, 1992). The development of NPs is an establishment of the “consequence” of the tolerance procedures of an organism into high-concentration specific metal. The biosynthesis of “Natural” biogenic metallic NP synthesis is divided into two major categories: (a) Bio reduction: Relatively strong models of metallic ions may be obtained by bio reduction reaction utilizing biological protocol resources and is obtained by dissimilar metal reduction. The metal ion has been oxidized and reduced by specific enzymes (Deplanche et al., 2010). (b) Biosorption: The metallic ions have been connected to the organism itself from an aquatic or soil sample. The ions of metal are binding to the peptides or cell walls chain were synthesized by bacteria and fungi after that these peptides chains are formed strong structures of NPs (Yong et al. 2002). Advantages of green or biological synthesise involve a non-toxic chemical used in biosynthesis, significant product, energy efficiency, low-cost production, good economic value, lowest waste, therefore, is called environmentally-friendly processes, competitive advantages, protect human health and fewer risks at biosynthesis time.

3. Microbial synthesis of nanoparticles by microbes

3.1. Fungi

Many fungal species have great ability for making different metal NPs which can be utilized in various processes. More than 6,000 biologically active compounds are recognized to be formed by filamentous fungal species especially (imperfect fungi and ascomycetes) and other fungal species (Bérdy, 2005). These microorganisms are extensively used as reducing and stabilizing agents, due to tolerance of heavy metal and the ability to bioaccumulate and internalize metals. In addition, fungal species can be simply developed on a broader scale (nanofactories) and can provide NPs with morphology and controlled-size (Khan et al., 2017). AgNPs

and AuNPs have been produced from various fungi, as seen in Table 1.

3.1.1. The mechanism of biosynthesis of NPs using fungi

3.1.1.1. Intracellular synthesis. In the case of intracellular synthesis, the metal primary is added to the culture and became interior the biomass. So, extraction of the NPs is wanted after the biosynthesis, employing chemical processing, centrifugation, and filtration to rid of the biomass and releasing the NPs (Molnár et al., 2018). The intracellular mechanism requires particular ion transportation in the fungal cell. In the intracellular biosynthesis of Ns, the cell wall presents an important role. The mechanism entails, electrostatic interaction of the positive charge (+) of the metal ions with the negative charge (-) of the cell wall. The enzymes link to the cell wall converts the ions into NPs, and these NPs are diffused across the cell wall (Nasreen et al., 2014). A stepwise mechanism for intracellular synthesis of NPs using *Verticillium* sp., this mechanism based on three steps, 1) trapping, 2) capping, and 3) bioreduction. It is an electrostatic interaction as the fungal cell surface contact with metal ions and traps the ions. The enzymes in the cell wall bioreduce metal ions to NPs of metal (Molnár et al., 2018). NPs synthesized using the intracellular system are smaller in size compared to the extracellular system synthesized NPs (Thakkar et al. 2010). The small size of NPs could be possibly due to the formation of particles inside the fungi. But NPs extraction processing becomes difficult and increasing the cost of NPs synthesis (Zhang et al. 2011). There are only a few studies that showed the intracellular synthesis of NPs by fungi such as *Phoma* sp. (Chen et al., 2003) for AgNPs and *Epicoccum Nigrum* (Sheikhloo et al., 2011) for AuNPs.

3.1.1.2. Extracellular synthesis. For the extracellular synthesis of NPs, numerous methods have been suggested by many researchers

(1) At first the method recommended was the steps linked to synthesize the CdNPs by *F. oxysporum*. The analysis of the protein examination to identify the existence of NADH-dependent reductase and responsibility for the reduction of Cd ions (Cd^{2+}) to the formation of CdNPs Ahmad et al. (2003).

(2) The second method of extracellular synthesis is the establishment by AgNPs were synthesized with the involvement of quinone and NADPH-nitrate reductase. In this case, both quinone and NADPH were provided to the electron needed to silver ion (Ag^+) and turn it into Ag neutral (Ag^0) Duran et al. (2005). (3) The third method of extracellular synthesis process of production of AgNPs requires the 1) NADPH and NADP are the principal roots of bioreducing and 2) hydroxyquinoline maybe works as an electron shuttle to move the electrons resulted due to the reduction process of Ag^+ ions to Ag^0 in the existence of nitrate reductase enzyme.

Table 2
Microbes mediated synthesized metallic NPs against plant pathogens.

Microbes	Metal NPs	Major Application	Plant Disease Management		References
			Pathogen	Host	
Fungi					
<i>Aspergillus niger</i>	Ag	Antifungal agent	Aspergillus flavus, Fusarium oxysporum		Al-Zubaidi et al., 2019
<i>Penicillium duclauxii</i>	Ag	Antifungal agent	Bipolaris sorghicola		Almaary et al., 2020
<i>Fusarium solani</i>	Ag	Antifungal agent	Aspergillus spp., Alternaria spp Fusarium spp.		Abd El-Aziz et al., 2015
<i>Trichiderma hazarium</i>	Ag	Antifungal agent	Alternaria/Alternata spp., Phytophthora arenaria		El-Moslamy et al., 2017
<i>Trichoderma longibrachiatum</i>	Ag	Antifungal agent	Alternaria alternata, Fusarium verticillioides		Elamawi et al., 2018
Bacteria					
<i>Bacillus cereus</i>	Ag	Antibacterial agent	Xanthomonas oryzae pv. oryzae		Ahmed et al., 2020
<i>Bacillus licheniformis</i>	Ag	Antiviral agent	Bean yellow mosaic virus		Elbeshehy et al., 2015
<i>Bacillus thuringensis</i>	Ag	Antiviral agent	Sun hemp rosette virus		Jain et al., 2014
<i>Bacillus siamensis</i>	Ag	Antibacterial agent	Xanthomonas oryzae pv. oryzae		Ibrahim et al., 2019
<i>Pseudomonas poae</i>	Ag	Antifungal agent	Fusarium graminearum		Ibrahim et al., 2020

The development of hydroxyquinoline is alike to that of quinones in electron transport. SDS- PAGE of fungal protein assured the occurrence of an enzyme (Kumar et al., 2007). Type of the fourth method is Michaelis–Menten kinetics (models of enzyme kinetics) aimed to synthesize the NPs wherever the reaction at start exhibits pseudo-zero order kinetics and then tracks higher-order kinetics. Consequently, at a starting state, the quantity of silver nitrate is greater, and when the reaction continues the quantity of silver nitrate reduces significantly, the biological reduction of various metallic NP was originated by a protein having amino acid with -SH bonds and probably the cysteine undergo the process of dehydrogenation on having a reaction with silver nitrate to form AgNPs. AgNPs will be cap by the free amino acid Mukherjee et al. (2008). The fifth method describes the involvement of multiple peptides or/and proteins is play important role in the bioreduction of metal ions, meaning surface-bound peptides/protein molecules acting as a stabilizing and reducing agent to the formation of AgNPs. FTIR spectra of different fungal species' culture the existence of amide I, II, and III groups. The same mechanism was applied with AgNPs by showing the reduction of silver ions by amide I and amide II groups, also AgNPs were stabilization by fungal protein (Sanghi and Verma 2009).

3.2. Bacteria

Bacteria have been easily applied as nanofactories to synthesize different NPs. Both the intracellular and extracellular methods have described.

Both extracellular and intracellular synthesis of NPs mainly involves oxidoreductase enzymes like (NADH-dependent nitrate reductase and NADPH-dependent sulfite reductase) and factor cellular of transporters. Extracellular biological synthesis ensues exterior to the bacterial cell after using various systems, for example (1) the bacterial biomass, (b) the supernatant of bacterial cultures, and (c) cell-free extracts. These mechanisms can be intracellular or extracellular synthesis metal NPs. AgNPs and AuNPs have been produced from various bacteria, as seen in Table 2.

3.2.1. Mechanism of NPs synthesis using bacteria

3.2.1.1. Role of enzyme and proteins. Most experiments have indicated the potential role of proteins and enzymes as the key bioactive moiety that works during the synthesis of NPs as a reducing and capping agent. Various defense systems have been adopted by Bacteria, viz. Dissimilatory oxidation, metal ion reduction, precipitation, complex formation to combat the toxicity of metals (Tanzil et al. 2016). Metal NPs are generated using redox reactions which happen both extracellularly and intracellularly. Metal nanoparticles are produced either intracellularly or extracellularly by redox reactions that occur. The potential presence of nitrate

reductases in metal bio reduction. Previous reports demonstrated a possible mechanism for the bio reduction of Ag^+ to Ag^0 using *Streptomyces* sp. LK3 at room temperature, this study obtained the nitrate reductase enzyme from *Streptomyces* sp. LK3 is responsible for biosynthesis (Karthik et al., 2014). Biosynthesis of AgNPs using *Alcaligenes faecalis* using NADH and NADH dependent reductases enzyme as reducing agent is responsible for bio-mediated synthesis of AgNPs (Divya et al., 2019). Bacteria like *Geobacter sulfurreducens* has pilin proteins as conductive to the extracellular synthesis of NPs. Pilin proteins found in bacterial external appendages has a significant function in transfer of electron and reduction to the formation of uranium nanoparticles (UNPs). In the absence of pilin proteins, uranium nanoparticles are formed inside the periplasmic space by intracellular synthesis. Pilin mode of action is significantly related to the biomineralization of uranium and extracellular synthesis of uranium nanoparticles (Reguera, 2012). This hypothesis based on AgNPs is synthesized by photoinduced electron transfer. Electron transfer through amino acids containing binding side chains like amides, aliphatic amines, alkyl groups, or alcohols have low binding energy with Ag^+ and allow to formation Ag^0 clusters and produce AgNPs by photoinduction. Hence, it was found that fast exergonic aggregation of Ag^0 into Ag^n groups was ultimately required for effective AgNPs (Reguera, 2012).

3.2.1.2. Role of electron shuttle quinones (or redox mediators). During NP synthesis, electrons can be transported through indirect reactions via a low molecular weight redox medium such as 1) NADH and coenzyme Q or 2) oxygen / superoxide or by direct interactions between cytochrome redox proteins and metal ions. Both cytochromes and redox mediators enhance extracellular metal NPs synthesis. *Shewanella oneidensis* MR-1 transferring electrons by 1) metal-reducing machinery by iron III oxides (Fe_3O_4) or 2) Mtr pathway (cytochromes and proteins) for transferring electrons from the inner to the outer membrane to the surface. In bacteria, metal NPs extracellular synthesis via a similar mechanism (Shi et al., 2012). To prove the concept of cytochromes role in the extracellular NPs synthesis, a *Shewanella oneidensis*, mutant strain, with deficient cytochrome genes was used to for the AgNPs synthesis. The resultant AgNPs were smaller in size and lower in number as compared to the wild-type strain of the same species. Hence, it was proved that cytochrome has a significant function in electrons transportation to extracellular metal ions (Ng et al., 2013).

Cytochrome has been shown to involve the direct participation of extracellular cytochrome protein complexes. Reduction of ferric citrate ($C_6H_5FeO_7$) and ferric acid (Fe_3O_8H) with *Geobacter sulfurreducens*, a bacterium that degrades minerals (Liu et al., 2014). In general, this report describes multi-component methods that operate individually or in complex ways to help electrons move from

the inner to the outer membrane and thus, aids in the synthesis of extracellular metal ions in NPs.

3.2.1.3. Role of exopolysaccharides. Bacterial cell that have multiple biological functionalities and have diverse biological functionalities, such as environmental tolerance, surface adherence, and cellular interactions produce and secrete bacterial exopolysaccharides (EPSs) (Rehm, 2009). EPSs have been investigated as agents for greener processing of various metal NPs because of their capacity to reducing metal ions to synthesize NPs and stabilizing them acting as capping agents (Cacchi et al., 2012). Rhamnose and pyranose sugars (EPSs) were reproductive factors in *Escherichia coli* for the formation of AgNPs. FTIR spectroscopy results from the interaction of EPS with metal ions showed that the two hemiacetal groups of the rhamnose and aldehyde groups in rhamnose and pyranose were related to the synthesis of AgNPs (Kang et al., 2014). Recently, a strategy was developed to synthesize AuNP using a pullulan polymer (EPSs) as a reducing agent. FTIR analysis certainly indicates that the basic structure of pullulan is not altered during AuNP synthesis by pullulan polymer, but that oxidation of fatty alcohol groups to pullulan polymer is important, correlating positively with the hypothesis that the gold ion (Au^{+3}) biosynthesis occurs.

Pullulan polymer oxidized CH_2OH groups to carboxyl group (COO^-) supporting bioreduction of Au^{3+} to Au^0 during the production of AuNPs (Choudhury et al., 2014). *Ochrobactrum rhizosphaerae* was used as a biosystem to synthesize and capping AgNPs and supported by EPS when its categorization by several biochemical methods proposed it as glycoprotein (GLP). Further, FTIR spectrum proved the involvement of functional group like the free CH_2OH group of GLP molecules were oxidized to a carboxyl group (COO^-) with synchronous bioreduction of Ag^+ to Ag^0 resulting in the synthesis of AgNPs (Gahlawat and Choudhury, 2019). In general, it has been observed that when metal ions bind to EPSs containing reducing sugars, they are chelated and then reproduced and stabilized by different functional groups. Polyanionic groups (having more than one negative charge) are well known chemical groups required in the biological absorption and stabilization of NPs.

4. Factors affecting biological synthesis of metal nanoparticles

The structural and geomorphological physiognomies of NPs can be managed by three main parameters viz. pH, temperature and reactant concentrations. These main parameters are essential for understanding the impact of environmental features on the synthesis of NP, they may play a significant part in the optimization of the synthesis of metallic NPs by biological templates.

4.1. pH

Generally, pH of the substrate and medium acts a fundamental role in control the shape and size of the NPs. The shape and size of NPs changing with the pH of the substrate or medium and large size NPs are generated at an acidic pH (Binupriya et al., 2010). Alkaline pH promoted the synthesis of AgNPs when silver nitrate was added to the cell filtrate of the fungus *Epicoccum nigrum* Qian et al. (2013). The fungus *Penicillium oxalicum*-Mediated synthesis of AgNPs with different pH range was examined. The finding showed alkaline pH produced AgNPs in a less synthesis time and smaller size distribution. These features indicate enhanced stability, due to the electrostatic repulsion of anions Du et al. (2015). Synthesis of AuNPs using *Aspergillus terreus* is controlled by pH. At pH 8, the shape of AuNPs converts from spherical to rod with an average size 20–29 nm. At pH 10, the average size of AuNPs

was in the range of 10–19 nm with a spherical shape. The gradual increase of pH leads to an increase in the reduction reaction so small synthesis AuNPs formed (Priyadarshini et al., 2014).

4.2. Effect of temperature

The temperature utilized in the production of AgNPs operating fungi could have a significant impact on main parameters such as the velocity of the synthesis and the stability and size of the AgNPs (Elamawi et al., 2018). The production rate of AgNPs by *Fusarium oxysporum* was increased at temperatures between 60 and 80 °C. Continuous increase of temperature manage fungal biomass secreted higher value of protein and acceleration of synthesis rate (Birla et al., 2013). *Aspergillus oryzae* used to production AgNPs, a high-temperature effect on the rate of production. If reaction starts at 30 °C temperatures can be complemented at 6 h but when used 90 °C for reaction can be finished after 10 min. while no synthesis occurred at 10 °C. meaning very significant temperature on the rate of production (Phanjom and Ahmed, 2017). No production of AgNPs was studied by utilizing the filtrate of *Rhizopus stolonifer* at 80 or 10 °C, which was accredited to the enzymes and support molecules may be denaturation or inactivation (AbdelRahim et al., 2017).

4.3. Effect of $AgNO_3$ concentration

In a great number of the various studies applying fungal species for extracellular synthesis of AgNPs, Silver nitrate ($AgNO_3$) was utilized at a quantity of 1 mM (Xue et al., 2016). In some studies, a lower concentration of metal precursor ($AgNO_3$) instigated in a smaller NPs size (Phanjom and Ahmed, 2017), but other studies achieved using the intermediate concentration of $AgNO_3$ leads to smaller sizes of AgNPs (AbdelRahim et al., 2017). Processing of the *Rhizopus stolonifer* to bio-template for AgNPs obtained the smallest AgNPs size (2.86 nm) at 10 mM $AgNO_3$, while sizes range from 54.67 to 14.23 nm were attained at 100 and 1 mM, correspondingly (AbdelRahim et al., 2017). The concentration of $AgNO_3$ affects the quantity of AgNPs generated not only AgNPs size. In research using *Fusarium oxysporum*, it was observed that the concentration of AgNPs improved as metal predecessor quantity developed between 0.1 and 1.5 mM, although no changes remained noticed at greater concentrations (Korbekandi et al., 2013).

5. Phytopathogens control by green synthesized nanoparticles

In different areas, including plant disease control, NPs have been used (Masum et al., 2019). In general, pesticides, along with symbiotic plants, animal species and human beings, are used selectively for parasites of crop plants without affecting plants themselves. Nevertheless, the indiscriminating usage of these chemicals/pesticides remains to be significant for environmental and societal concern (Kutz et al., 1991). Furthermore, the production new strains of pathogenic is a progressive concern, the chemical or pesticide implementation is costly and not always successful. Currently, development in the field of green synthesis has encouraged researchers and scientists to use its ability against pathogenic microorganisms. Biosynthesized metallic NPs such as, gold, silver, zinc and copper, have been reported against many species of pathogenic microorganisms such as Gram-negative bacteria, Gram-positive and some fungal species. The silver NPs get more support owing many biological sources which usage for green synthesis such as fungi, bacteria or plants (Nisar et al., 2019). Nanotechnology has potential opportunities in different ways in plant pathogenic treatment. The raw usage of NPs to seeds or

foliar spray against plant disease causing agents, that are more severely repressed, as likened to other chemical released by pesticides, is the most widely used process. In another side nanomaterials are used as carrier materials of chemical active ingredients for the controlled release of pesticide products. (Mujeebur & Tanveer 2014). A list of NP-dependent researches for plant disease control is presented in Table 2.

6. Mechanisms of nanoparticles against plant pathogenic microorganisms

The precise mode of action of NPs is not well known, against phytopathogens. Some processes have been documented to date, such as protein disruption (Hajipour et al., 2012), production and antioxidant degradation of reactive oxygen species (ROS), membrane disability work (e.g., disruption to membranes, lack of membrane permeability), genotoxicity, and transporter gene expression inhibition (Lemire et al., 2013). These pathways cannot work independently, but act against different phytopathogens in combination. The electrostatic attraction accrues bacterial cell membranes and negatively charged NPs as negative or positive charges decrease, causing NPs to adhere to the cell membranes. The morphological properties of membranes affected by NPs and membrane depolarization disrupt membrane permeability and respiratory activity, and ultimately lead to damage to cell components, resulting in death. This breakdown of cellular structures causes the leakage of substances inside the cell, including enzymes, proteins, metabolites and DNA. In addition, NP can create irregular holes in the cell walls of microorganisms to facilitate penetration of NPs into extracellular and intracellular spaces (Alghuthaymi et al., 2015). NP behavior of membrane damage and cell surface perforations formed can be observed using TEM. TEM exhibits severe disruption of cell walls, leakage of nuclear and cytoplasmic material, and swelling. It causes bacterial death. (Masum et al., 2019, Ibrahim et al., 2020). Related effects with AgNPs have also been found in several other plant fungi, such as *Alternaria alternata* and *Trichosporon asahii*. NP toxicity can occur due to ROS formation (Xia et al., 2016). Free radicals can destroy cell walls and various biological molecules like cell wall, proteins, fats, and DNA. DNA damage can occur, for example deletions, mutations, and single strand rupture, double strand breakage, and protein crosslinking (Soenen et al., 2011). Antimicrobial pathways include cell membrane damage and ROS formation (Zhang et al., 2018). Cell membrane damage and AgNP were detected in *Azotobacter vinelandii* cells by TEM and AgNP-induced hydroxyl radicals were detected in bacterial cells using electron spin resonance.

7. Environmental risks of nanoparticles

In addition to this benefit, certain harmful or harmful impacts of such NPs on different factors of the ecosystem can be revealed in many studies that NPs may be utilized to monitor or regulate plant disease causing agents (Worrall et al., 2018). The NPs that were utilized for controlling plant pathogens may be dispersion from the agricultural land to the soil, water and atmosphere. The dispersion can transport by air and can occur leaching, surface run-off by rain, (Morales-Díaz et al., 2017). Therefore, in agriculture treatment by nanomaterials is required a standard usage for ecologically sustainable and safe environment. The use of NPs for the treatment of plant pathogens. Knowledge of potential risks for direct or indirect application to crop plants and the ecosystem in which crop plants interact with animals, microorganisms or humans should be accompanied. The use of NPs for the treatment of plant pathogens. Knowledge of potential risks for utilization on crops and interaction with ecosystem which the plants have.

Declaration of Competing Interest

The authors declare no conflict of interest.

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