



A Compendium on the Eco-Sustainable Biosynthesis of Palladium Nanoparticles (PdNPs) and Their New Avenues Towards Environmental Applications

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ABSTRACT

Palladium Nanoparticles (PdNPs) are considered significant catalytic agents, along with a wide range of applications, mainly hydrogen storage and sensing, biomedical imaging, and remediation strategies. Extensive studies are being carried out on the formation of PdNPs (PdNPs) worldwide, showing the predominance of the chemical approach among various technologies for the synthesis. The traditional chemical method employed in the formulation of PdNPs contains certain limitations that have been overcome by the use of the alternative biological method, as they are meek, low-cost, and benign to ecosystems. Therefore, the present review provides an overview of the modernized techniques involved in the biological approach for PdNPs formation by utilizing various natural origins, for example, plants as well as microbes, for their enhanced stability and applications in fields of the environment. Various mechanisms and parameters involved, along with approaches utilized for the characterization of bioPdNPs, are described, with an insight being delivered on the utility of biologically synthesized palladium nanoparticles. Recovery of PdNPs to achieve a circular economy is also being focused. In addition, the future prospectus on palladium nanoparticle research is also summarized.

INTRODUCTION

Palladium is considered one of the most extensively utilized precious, switching metals that displays typical physico-chemical, optical, and thermodynamic characteristics at the nanoscale margin (Watanabe et al. 2006, Cheong et al. 2010). Although the metal palladium has been the interest of researchers since ancient times, its revitalization as PdNPs has resulted in a substantial enhancement in the context of various biotechnological applications through emerging nanoscience and nanotechnological aspects. Moreover, PdNPs imparts great attention because of their utility as a catalyst in coupling reactions (Karimi & Enders 2006), Heck reaction (Heck & Nolley 1972), Kumada reaction (Jana et al. 2011), Sonogashira reaction (Sonogashira 2002), Negishi reaction (Astruc 2007), Stille reaction (Milstien & Stille 1978), Buchwald-Hartwig reaction (Widenhoefer & Buchwald, 1996), hydrogenation reactions (Wilson et al. 2006), and fuel cell reactions (Zhang et al. 2011). They are also considered good catalysts in both homogeneous and heterogeneous reactions as they possess enhanced surface-to-volume ratios with great surface energy (Narayanan & El-Sayed 2005). Moreover, PdNPs performs a vital part in several biotechnological fields, such as the production of pharmaceutical compounds, degradation of harmful environmental pollutants (Kora & Rastogi 2016, Martins et al. 2017, Safavi & Momeni 2012), and preparation of non-enzymatic biosensor to detect hydrogen peroxide in milk (Baccar et al. 2013).

An analysis of PdNp's applications through region-wise market study depends on various factors. They are mainly consumption, its growth significance, market share between competitive nations, and their adopted technologies. The top 5 competitive regions that are involved in its manufacture and applications are North America, Europe, Asia Pacific, Latin America, and the Middle East and Africa, according to data provided by the Worldwide "PdNPs market" Research Report 2024. Their major trends involved the use of PdNPs in medical diagnostics, sensors, fuel cells, and catalysis (environmental usage). They are globally demanded as vehicle exhaust catalysts in the automobile sector. They also act as catalysts for degrading hydrocarbons in petroleum sites. U.S. plays the dominant role, succeeded by Germany and the U.K. North America and Europe contribute about 45% of the market share, followed by China and Japan, around 30 %. Finally, Latin America, and Middle East & Africa follow the path by accounting for around 15 % of the market share, and the remaining is contributed by Brazil and Saudi Arabia.

An extensive variety of wet chemical methods, *viz.*, polyol (Xiong et al. 2005a), sonochemical (Nemamcha et al. 2006), electrochemical (Cha et al. 2007), as well as chemical reduction (Nguyen et al. 2010), have been explored for the morphologically regulated formation of PdNPs. The catalytic function of palladium is determined by its structure at the nano level (Xiong et al. 2005b). Hence, the formation of uniform-sized palladium colloidal particles has been considered an essential matter in research. Several approaches, particularly uniform-shaped palladium particles in aqueous solutions by a wide variety of stabilizing agents, have been used by researchers (Ganesan et al. 2007). Fig. 1 shows the traditional methods for materializing PdNPs.

Among various techniques, the chemical method is widely used, where the salts of metallic precursors are reduced to metal atoms by utilizing various reducing agents, *viz.* citrate, hydrides, ethylene glycol, and hydrazine, all of which pose serious risks to the environment and health of living beings. Hence, there is an increasing demand aimed at the development of a clean, nontoxic, and ecological synthetic approach. The expansion of enhanced production and inexpensive technology for nanoparticle creation is a crucial task. To date, the enormous variety of microorganisms, involving prokaryotes and eukaryotes, has been accounted for the formation of nanobiomaterials (Basak et al. 2014, Basak et al. 2020). Although reports are there on its biosynthesis and applications, reports are still scanty on its mechanism of synthesis through microbes and the 'RRR' concept. The author has tried to portray this information about PdNPs from its cradle to grave. Probably this is the first report to go through a compendium including the aforementioned aspects, challenges, and benefits of environmental cleanup as well.

Therefore, the current study envisages the overall technology applied for the sustainable preparation of PdNPs throughout the last decade. The objective of the refurbished report is also to consolidate various literature about PdNPs' utilities in several fields involved in environmental applications. Moreover, the review tries to envisage prospects, challenges, and research facilities regarding the particular area of interest. Furthermore, the recovery, recycling, and reuse ('RRR') are also discussed in the particular comprehensive review.

MATERIALS AND METHODS

The compendious review of literature involves the critical

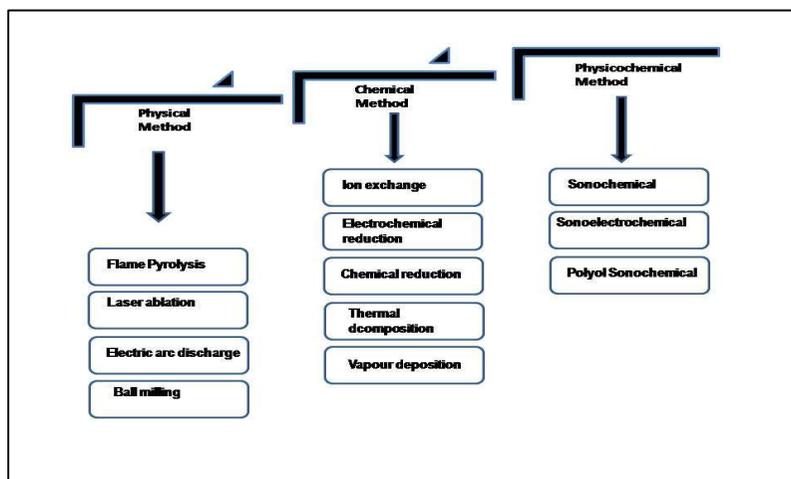


Fig. 1: Traditional methods for materializing PdNPs.

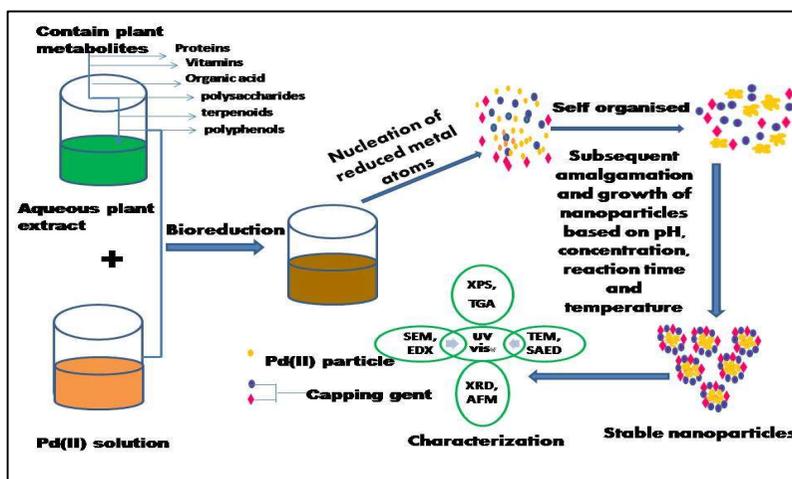


Fig. 2: General route for the biological formulation of nano-biopalladium through plant metabolites.

exploration of the extensive literature review and research papers existing over the last two decades with respect to palladium nanoparticle biosynthesis and its utilities. The comprehensive study used the exploration of different websites like JSTOR, INFLIBNET, Scopus, Google Scholar, and Science Direct through combined keywords such as “palladium biosynthesis”, “characterization, properties”, “environmental application,” and “recovery, recycle and reuse”.

Biosynthesis of PdNPs

Owing to the drawbacks in the physico-chemical synthesis of the PdNPs with respect to their maintenance, the discharge of perilous waste or the formation of Pd nanomaterials by using chemical agents pose hindrances in their application in the clinical fields (Manjare et al. 2021). The biological formation of PdNPs has proven to be an alternative advantageous path. This has contributed to the attainment of sustainability with better results in the formation of products along with their advanced properties. Various biological agents, *viz.*, plant extracts, microorganisms, and biological products of the microbes, are used for the synthesis of PdNPs

Biological Formation of Nano-Palladium by Using Plant Extracts

The biological process involving plant extract is found to be an uncomplicated and adaptable technique followed during the formation of PdNPs (Fig. 2).

Owing to its advantage over the traditional process, researchers have shifted their interest towards the effective utilization of diverse compounds obtained from plants. An overview of PdNPs synthesized biologically is given in Table 1.

For the biosynthesis of nano palladium, the chosen extract of the plant will be mixed with palladium salt solution at a specified concentration under ambient conditions in a single-step experiment (Fig. 2). In the absence of any stabilizer or capping agent from outsource, these active biological compounds obtained from plants acts both as reducer as well as stabilizer. Furthermore, the reaction mixture will be carried out for the reduction of metal salt to a visual color alteration. The phytochemicals/ metabolites extracted from various plants used for PdNPs formation are polyols, polyphenols, flavonoids, vitamins, organic acids, polysaccharides, terpenoids, and proteins. These particular plant extracts are reported to biogenically synthesize nanosized Palladium particles (Qazi et al. 2016).

Microbe-Mediated Synthesis of Nano-Palladium Particles

Nano-sized palladium particles formed by microbial factories have come out as a promising complementary method that demands achieving environmental sustainability with enhanced strength and controlled morphology of nanoparticles (Shedbalkar et al. 2014). Several experiments using various bacteria (a palladium-compatible agent) were conducted to elucidate the mode of action implicated in the materialization of nano-palladium particles (Abbasi et al. 2023, Sharma et al. 2023). Therefore, the possible way for the formation of these nano-sized Palladium particles through microbes can be elucidated in two ways, *viz.* (i) intracellular mode of action and (ii) extracellular mode of action (as shown in Fig. 3).

Intracellular mode: Here, the PdNPs remain concentrated within the cell cytoplasm so that they can sustain their reliability while the process is being carried out. There

Table 1: Biological formation of nano-biopalladium through different bioreductants/ biostabilizers from plants.

Plant as bioreductant/biostabilizer	Size and shape	References
<i>Dioscorea bulbifera</i>	2.0-5.0 nm, globular	Ghosh et al. 2015
<i>Cinnamom zeylanicum</i>	15.0-20.0 nm, spherical	Satishkumar et al. 2009a
<i>Cinnamon camphor</i>	3.2-6.0 nm, quasi-spherical	Yang et al. 2010
<i>Curcuma longa</i>	10.0-15.0 nm, spherical	Satishkumar et al. 2009b
<i>Musa sp. (banana)</i>	50.0 nm, distorted, crystalline	Bankar et al. 2010
<i>Glycine max</i>	15.0 nm, spherical	Vivekanandhan et al. 2009
<i>Hippophae rhamnoides</i>	2.5-14.0 nm, spherical	Nasrollahzadeh et al. 2015
<i>Camellia sinensis</i>	5.0-8.0 nm, spherical	Lebaschi et al. 2017
<i>Terminalia bellirica</i>	30.0-45.0 nm, triangular	Viswadevarayalu et al. 2016
<i>Prunus X yedoensis</i>	50.0-150.0 nm, spherical	Manikandan et al. 2016
<i>Catharanthus roseus</i>	38.0 nm, spherical	Kalaiselvi et al. 2015
<i>Moringa oleifera</i>	10.0-50.0 nm, spherical	Anand et al. 2016
<i>Anacardium occidentale</i>	2.5-4.5 nm, spherical	Sheny et al. 2012
<i>Artemisia annua</i>	20.0- 30.0 nm	Naushad et al. 2015
<i>Stachys lavandulifolia</i>	5.0-7.0 nm, spherical	Veisi et al. 2015
<i>Pulicaria glutinosa</i>	20.0-25.0 nm, globular, crystalline	Khan et al. 2014
<i>Anogeissus latifolia</i>	4.8 nm, cubic crystal	Kora & Rastogi, 2018
<i>Eclipta prostrate</i>	18.0-64.0 nm, spherical	Rajakumar et al. 2015
<i>Annona squamosa</i>	80.0-100.0 nm, spherical	Roopan et al. 2011
<i>Gardenia jasminoides</i>	3.0-5.0 nm, polyhedral	Jia et al. 2009
<i>Euphorbia granulate</i>	25.0-35.0 nm	Nasrollahzadeh & Sajadi, 2016
<i>Asparagus racemosus</i>	1.0-6.0 nm, cubic	Raut et al. 2013
<i>Coffea arabica</i>	20-60 nm, cubic symmetry	Nadagouda & Varma, 2008
<i>Azadirachta indica</i>	5.0-50 nm, small and large spheres	Joseph et al. 2014
<i>Phoenix dactylifera</i>	5-21 nm, small and spherical	Tahir et al. 2016
<i>Ananas comosus</i>	1-16 nm, spherical	Olajire & Mohammed, 2019
<i>Salvia hispanica</i>	9.0-20.0 nm Semi-Spherical	Kiani et al. 2020
<i>Urtica</i>	3.0-12.0 nm Irregular	Gulbagca et al. 2021
<i>Cissus quadrangularis</i>	12.0-26.0 nm Spherical	Anjana et al. 2019
<i>Peganum harmala</i>	16.0-32.0 nm Spherical	Fahmy et al. 2021
<i>Fritillaria imperialis</i>	20.0-30.0 nm Quasi-spherical	

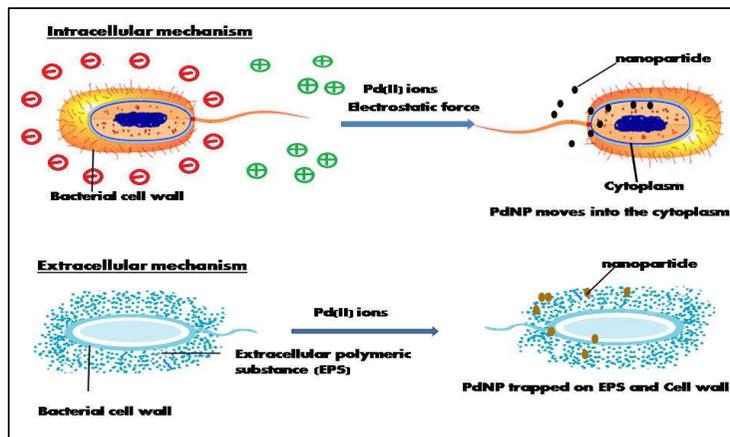


Fig. 3: Mode of action involved in the microbe-mediated nano-palladium particle formation.

are reports on bacteria (*B. benzeovorans* NCIMB 12555, *D. desulfuricans* NCIMB 8307, and *D. desulfuricans* NCIMB 8326) for the residence of approximately 8 nm sized icosahedral PdNP particles (Omajali et al. 2015). The possible stepwise mechanism for the intracellular method might be through trapping electrostatically, bioreduction, nucleation, and capping (Nasreen & Taranath 2014). Recently, scientific reports have demonstrated the intracellular microbial-mediated formulation of nanoparticles from various non-precious metals *viz.* iron (Peng et al. 2010); copper (Navarrete et al. 2011); Chromium (Polti et al. 2011, Ravindranath et al. 2011); uranium (Sousa et al. 2013). However, to date, information about the formation of intracellular palladium is very limited. E.g., intracellular palladium is situated within the inner membrane (Foulkes et al. 2011). Although microbes act as the biogenic bearers of palladium, whose valency is converted from 2^+ to 0, they lose their viability, but still, *E. coli* could remain physiologically activated with the inability to proliferate (Joudeh et al. 2021).

Extracellular mode: Here, the palladium colloidal suspension is present over the outer wall of the periplasm, plasmalemma, or surface of the cell wall, especially on the extracellular polymeric substance can be observed. Several reports have been conveyed on the use of a wide range of bacteria, *viz.* *Shewanella sp.* (Windt et al. 2005), *Desulfovibrio sp.* (Yong et al. 2010), *B. Megatarium* (Chen et al. 2023), and for shifting the oxidation phase from +2 to 0 of PdNPs lying over the periphery of the cell. Thus, it makes the metallic ion nontoxic, along with suitable retrieval of nanoparticles without cell destruction. The basic mechanism for the extracellular formation of PdNPs is through the microbial hydrogenase enzyme (Yang et al. 2020). The formation of bio-nano-palladium particles by members belonging to the groups of fungi (Tarver et al. 2019) has been reported so far. Few algae, *viz.* *Chlorella vulgaris* (Arsiya et al. 2017) and *P.boryanum* UTEX 485

(Maggy et al. 2007) are being used to make nano-palladium particles. Table 2 shows the collection of microbes for PdNPs formation.

PdNPs Synthesis Through Biological Products

Apart from the microbial synthesis of PdNPs, the usage of secondary metabolites regarding the development of PdNPs gives budget-friendly solutions for the attainment of a safer Earth. Among biomolecules, nucleic acids such as RNA serve as great biogenic catalysts for the formation of palladium nano-bio-conjugates with controlled morphology (Liu et al. 2006). DNA in double-stranded form, compared to single-stranded one, proves to be an efficient biocatalyst. They make minimum-sized nanoparticles with greater reducing capability of H_2O_2 and oxidizing capacity of ascorbic acid (Fang et al. 2007).

The utilization of high molecular weight biomolecules, *viz.* protein, polypeptide, and amino acid varied sequences for stabilization of peptide chains has been reported to ensure a substantial influence over nanomaterial structure. An amino acid residue can perform a dual role in increasing stability while reducing it simultaneously. Zhou et al. (2016) showed the potential of biofilm-producing natural polymer externally bearing functional groups that would attach or stabilize PdNPs. Continuous production of PdNPs by exploiting a denitrifying biofilm encouraged the creation of zerovalent Pd from divalent Pd. Both enzymatic as well as autocatalytic conversion of the ion is carried on top of the outer layer of concave-fiber membranes so as to carry (H_2) for electron donation. Several exopolysaccharides, like xanthan gum, obtained by fermentation of the bacterium *Xanthomonas campestris*, act both as a reducer and stabilizer for materializing PdNPs of 10 nm size (Kumari et al. 2015). This nanomaterial stabilized by the aforementioned polysaccharide served as an excellent hydrogenating property in converting 4-nitrophenol to 4-aminophenol using borohydride. Hormones and vitamins, *viz.* ascorbic

Table 2: Synthesis of nano-palladium using microbes.

Bacteria	Size/shape	Reference
<i>Pseudomonas sp.</i>	4.0-20.0 nm	Schluter et al. 2014
<i>Shewanella oneidensis</i>	irregular	Windt et al. 2005
<i>Clostridium butyricum</i> , <i>Citrobacter braakii</i> , <i>Enterococcus faecium</i> , <i>Bacteroides vulgates</i>	irregular	Hennebel et al. 2011, Ghosh 2018
<i>Bacillus benzeovorans</i> , <i>Bacillus sphaericus</i> , <i>Desulfovibrio desulfuricans</i>	9.0-12 nm, icosahedral	Omajali et al. 2015
<i>Geobacter sulfurreducens</i>	14.0-25.0 nm	Matthew et al. 2013
Microalgae		
<i>Chlorella vulgaris</i>	5.0-20 nm, crystalline	Arsiya et al. 2017
<i>Plectonema organum</i>	≤ 30 nm, spherical and elongated	Maggy et al. 2007

acid (Ameri et al. 2020) and oxytocin + amino acid (Bendre et al. 2020), have recently acted as potential agents for the synthesis of the target material. Clergeaud et al. (2013) depicted that lipid glycerol monooleate, along with the tetrachloropalladate solution, synthesized 4 nm-sized PdNPs. This is mainly accompanied by a polyol-type reaction where the palladium is formed from the reduction of palladium through a hydroxyl group present in glycerol at 25°C.

Significant Parameters for PdNPs Synthesis

Important parameters considered for the regulated synthesis of PdNPs are as follows: (i) pH, (ii) the type and amount of the stabilizing agent used, (iii) the relative concentrations of both metallic precursor and reducing agent, (iv) the variation of reaction temperature and (v) using of foreign ions (Cheong et al. 2010).

The optimized pH for the development of PdNPs using 45.0 ml of *Prunus xyedoensis* leaf extract with 0.1 M palladium (II) chloride solution is 7.0 (Manikandan et al. 2016). The appearance of palladium nanomaterials varies based on the nature of different stabilizing agents that cap on the same-shaped palladium nuclei. The precursor PdCl₂ was reacted with ethane 1,2-diol in an argon atmosphere using polyvinylpyrrolidone as stabilizer synthesized round-shaped, 7.5 nm apparent-sized PdNPs. Approximately 8.4 nm sized and polyhedral-shaped PdNPs in the atmosphere, along with 6.3 nm sized particles in the presence of argon, were obtained in a mixture of amphiphilic compounds (PVP and CTAB), respectively. The ratios of metallic precursor along with the reducing agent have been found to play a crucial role. A higher reductant concentration might result in an enhanced reduction rate of change in the morphology of nanomaterials (Xiong et al. 2007). The size of the nano-palladium can be transformed based on the different preliminary concentrations of PdCl₂ over amine. The reaction temperature is one of the main factors that not only affect the reduction rate of metal precursor but also bring about morphological change in Palladium nanomaterials. Guisbier et al. (2011) explained the consequences of various temperatures triggering changes in the geometrical shape of PdNPs. Several works have emphasized the influence of foreign species (trace metallic ions) on the control of the shape formation of PdNPs. The addition of trace metal ions mainly facilitated the self-assembly, in addition growth of the nanoscale materials too (Cheong et al. 2010). Manikandan et al. (2016) mixed leaf extract and Pd(II) at a ratio of 40:5 to obtain green nano palladium particles. Parameters have been depicted in Fig. 4.

Properties and Characterization of BioPalladium Nanomaterials

Properties: PdNPs have interesting properties compared to the metal ion itself, which contributes to immense medicinal applications. The properties are (i) efficient catalytic activity (Prashant et al. 2006), (ii) physicochemical properties (Yang et al. 2006), and (iii) optical and electronic properties. Recently, a wide number of investigations were carried out to find novel approaches for PdNPs synthesis with improved properties. Due to their catalytic and/or optical properties, they have several environmental applications that will be discussed in the review. Though PdNPs impart excellent mechanical and chemical stability, they are still thermodynamically unstable because of the accumulation of nanoparticles in a reaction mixture. This might be a general process that might lead to complications while studying its properties and usage. A wide range of chemicals, like polymers, ligands, dendrimers, and tensides, are being reported to reduce and stabilize PdNPs (Cookson 2012). Electrostatic force of attraction or a combination of the two, i.e., oppositely charged forces, might be the reason for stabilization.

Characterization: Biologically synthesized PdNPs can be observed through various instrumentation techniques. A series of analytical techniques must be used to determine the character of the material. Starting with the colloidal suspension, the color change of the synthetic solution to brownish back from orange confirms the formation of PdNPs. These biopalladium nanomaterials are initially detected by a UV-Vis spectrophotometer. FT-IR spectral analysis is being used in various biological agents to spot the charged groups occurring over the superficial material required for the addition of electrons to metallic Pd. Further, the crystal structures of the formed PdNPs are investigated by XRD-spectroscopy (Bankar et al. 2010). Nanomaterial has a different structure (different phase) than their bulk version (crystal). A detailed diffraction study illustrates that the most significant peak is due to the crystal unit cell structure of PdNPs. The elements present and characterization of a nanoparticle are being analyzed using the instrumentation technique of energy dispersive X-ray (Omajali et al. 2015). Both elemental analysis and surface characterization can be analyzed by X-ray photoelectron spectral (XPS) techniques. The difference in kinetic energy from the similar dispersed states of the particle size, derived from the varying magnitude of experiments between different core levels, determines the morphology of particles. Optionally, the average size of the particle can also be analyzed from a fraction of monolayer and crystallite samples on a concentration basis. In the case of the formation of nanoparticles located intracellularly, the dimension of the nanoparticle is very minimal. This can be voluntarily visualized in Transmission

electron microscopy. Therefore, it is necessary to analyze electron backscattering and confirmatory analysis via EDX analysis. In addition, it may also show the existence of carbon and oxygen peaks, inferring the occurrence of these elements on the exterior of PdNPs. Furthermore, the capping effort of organic molecules can also be confirmed during the biosynthesis of PdNPs through EDX analysis (Tahir et al. 2016). Identification of palladium, phosphorus, and sulfur within *D. desulfuricans* and *B. benzovorans* cells was illustrated by EDX (Omajali et al. 2015). Further existence of these particular elements was established by Scanning transmission electron microscopy (STEM) that visibly revealed the entrapped miniature-sized particles within the bacterial cells. The morphological appearance and dispersion of nanopalladium are visualized by SEM and TEM. The internal structural elucidation of the particle, mainly crystallinity and lattice structure, is noted by TEM by observing electrons transmitted from the sample. The surface topography and its organization, depending on its functionality, are determined by SEM. The crystalline structure and size of PdNPs are further investigated through high-resolution TEM (HRTEM) - selected area electron diffraction (SAED). A schematic diagram presenting the factors, properties, and characterization of PdNPs is highlighted in Fig. 4.

Environmental Applications of PdNPs

The rapid expansion of the concentration of the contaminants released into the commercialized world poses a threat to living beings. Hence, the researchers are trying to combat these problems through several modern attempts, like the use of external stabilizing agents, as various biological constituents extracted from floras and microorganisms can act solely as stabilizing as well as capping agents.

Several works have reported that bacteria-attached catalytic nanoparticles may show equivalent or better effective catalysts compared to other conventional catalysts involved in photodegradation procedures (Behera et al. 2019) to remove nitro compounds and organic dyes (Edal et al. 2024). Environmental application of biologically synthesized PdNPs mainly focuses on the environmental clean-up of various contaminants. These have been discussed in the following sub-sections.

Removal of dyes: Enhanced modernization and industrial activity have generated the discharge of dyes that have hazardous effects on the ecological balance of the Earth. Therefore, several efforts are being made to eliminate these dyes. The synthesized biopalladium nanomaterials using exudates of *C. roseus* leaves in broth suspension showed an enhanced photocatalytic role in degrading phenol red dye at an optimized pH of 8.0 (Kalaiselvi et al. 2015). In one of the reports, hollow PdNPs-activated biofilm showed better elimination of azo dyes and methyl orange dye present in wastewater by obstructing the kinetic barrier (Kalathil & Chaudhuri, 2016). Decolorization of dyes such as methyl orange, acid blue, reactive black, and acid red at an approximate range of 70 % is observed by viable *Klebsiella oxytoca* with Pd (Wang et al. 2018). This might be due to its enhanced catalytic property and increased transfer of electrons outside the cell membrane region. The utility of complex Pd/Fe₃O₄-PEI-RG nanohybrids for wastewater treatment by mineralization of several contaminants stimulated through catalysts has enticed the interest of recent researchers. These nanohybrids showed excellent breakdown of methylene blue with a significantly enhanced removal of over 99% through sodium borohydride within the reaction mixture. Simultaneously, the nanoparticle could be detached from the

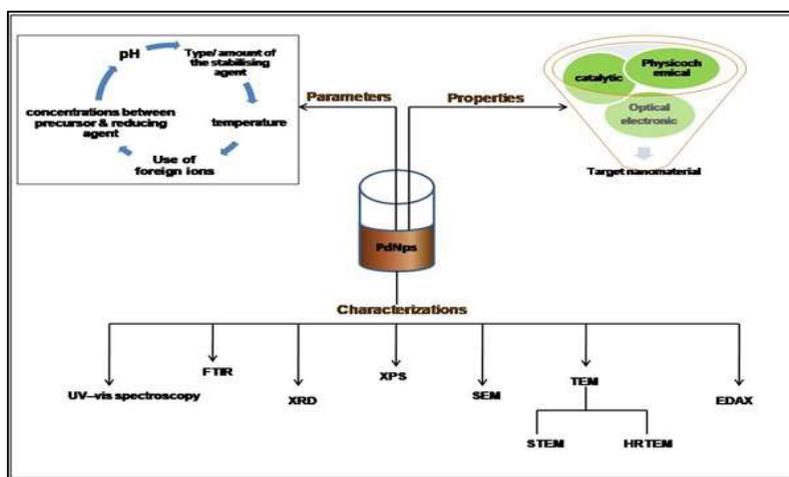


Fig. 4: Properties and instrumental analysis of nano-palladium particles.

synthetic solution in the presence of the magnetic field applied externally. These nanomaterials can be reused after being cycled nine times without any potential effect on their catalytic activity. Therefore, these qualities enabled this catalyst to be an encouraging contestant in the arena of energy and environment (Li et al. 2015).

Removal of nitrophenol: Nitrophenols are one among various contaminants that lead to cancer and must be reduced to aminophenols. Experiments have been conducted by using *Phoenix dactylifera* synthesized PdNPs for the degradation of 4-nitrophenol to 4-aminophenol in the presence of a catalyst within 2 min, thereby forming a 4-nitrophenolate ion intermediate (Tahir et al. 2016). Palladium-loaded hydrogel conjugates (PEI/Pd) reduce 4-nitrophenol to 4-aminophenol in wastewater (Feng et al. 2020). In 2021, Advanced nanoparticle formation core-shell nanomaterial Fe₃O₄@CS-Starch/Pd for mineralization of 4-nitrophenol in the presence of ultrasound waves. After the recovery process, the catalyst was utilized for consecutive repeated cycles (Veisi et al. 2021). Certain nanomaterials are used for dual catalytic application in removing nitrophenol as well as dyes simultaneously. Anand et al. (2016) showed the catalyst-oriented degradation of organic pollutants like para-nitrophenol (PNP) and methylene blue present in industrial effluents by biosynthesized PdNPs from *Moringa oleifera* flower extract. The green technology used for the formulation of PdNPs utilizing *Anogeissus latifolia* (gum ghatti) showed better antioxidant activity even at a minimum quantity. The particle also possessed efficient catalytic properties while reducing several dyes like methylene blue, coomassie brilliant blue G-250, methyl orange, and 4-nitrophenol through sodium borohydride. A single-pot, cost-effective technology was established for palladium nanoparticle materialization using a biocompatible polymer named gum olibanum obtained from *B. serrata*. This bifunctional agent reduces and stabilizes the nanomaterial simultaneously. Spherical-sized nanoparticles ranging from 2.5–8.8 nm were resistant to bacteria with different cell walls, even at high concentrations. They also imparted antioxidant activity. The nanoparticles showed homogeneous catalytic activity by reducing the aforementioned dyes. Therefore, these dyes revealed degradation activity for brilliant dye and pigment (Kora & Rastogi 2016).

Removal of pesticides and heavy metals: Pesticides are one such pollutant that, upon being discharged into the effluent or solid waste, cause harm to human health. Biosynthesized Palladium-sized particles effectively degrade dehalogenated PCBs (Windt et al. 2005), perchlorate and nitrate (Windt et al. 2006), PBDEs (Harrad et al. 2007, Deplanche et al. 2009), trichloroethylene (TCE) (Hennebel et al. 2009), lindane

and chlorobenzenes (Mertens et al. 2007), and diatrizoate (Hennebel et al. 2011), and chlorpyrifos and tebuconazole (Hamid et al. 2024). Chromium Hexavalent ion is a serious contaminant that must be reduced to trivalent chromium so that it can be used for various metabolic activities. Productive formation of ferric oxide conjugated palladium nanobioparticles could eliminate hexavalent chromium to trivalent chromium in the synthetic liquid environment in the presence of formic acid (Kalantari et al. 2021).

Removal of antibiotics: Essential pharmaceutical components like antibiotics are being utilized by patients at around 30 %, and the rest remain deposited in wastewater or sludge due to human excretory activities. Thus, it is important to take the necessary steps to reduce the dispersion and aggregation of relentless antibiotics into the ecosystem (Gavrilescu et al. 2015). Ciprofloxacin is one such antibiotic that induces mutation, as well as cancer, and has been linked to the incidence of hydrogen. The ciprofloxacin and hydrogenated palladium ion conjugates are removed at an approximate range of 88.0%. The presence of hydrogen boosts the sequestration of the pollutant by the conjugate (He et al. 2020). However, a different method was used for its removal in the presence of microbes. *Desulfovibrio vulgaris* synthesized PdNPs because of sulfamethoxazole (Martins et al. 2017).

Challenges

BioPdNPs dominate other processes in terms of cost and scalability, but there may be certain challenges that can be addressed. They are not monodispersed, and the rate of production is not speedy (Prasad et al. 2020). They may show irregular, uniform surfaces (Matsena & Chirwa 2021). Crucial parameters, *viz.*, localization and morphology of nanoparticles, depend on microbial species. Biomolecules are involved in the process; hence, nanomaterials may be of different sizes (Filice et al. 2021). It may harm seed germination and accumulate in living organisms of the environment (Xiaodi et al. 2024). With the increase in the use of PdNPs for controlling automobile exhaust pollutants, an imbalance in biogeochemical cycles may occur. So, risk analysis of palladium is crucial to regulate its utility as a catalytic converter to obtain a sustainable Earth (Aarzo & Nidhi 2022).

Recovery of Palladium Towards the Achievement of Circular Economy

Economic upliftment requires commercialization that consequents in pollution of the ecological system because of the disposal of toxic metals. Hence, technologies must be there to recover, recycle, and reuse them, especially certain

heavy metals, *viz.* Au, Ag, Pd, etc., are precious in terms of cost and various applications such as catalyst hydrogenation, oxidation, dichlorination, gas sensing, and hydrogen storage (Klinkova et al. 2017). Moreover, eco-friendly processes must be applied to recover a high rate (~99.0 %) and purity of palladium through the union of copper capture and electrodeposition technique in the presence of 0.5 molar nitric acid, which had no adverse effect on the environment (Liu et al. 2020). Speedy, cheap, and eco-sustainable methods are to be involved in the recycling and recovery of the PdNPs so that they can be reused. For example, the pulsed laser ablation process is a powerful and energetic process that can isolate nanoparticles within 30 min of its irradiation (Lee et al. 2021). Recently, microbes have been used in the formulation of nanoparticles. Although heavy metal hazards affect microbial life, they can still be combated by diffusing the toxicity of metals through their actions at the gene and protein levels (Veisi et al. 2016, Patel et al. 2021, Law et al. 2022). Economically profitable and sustainable technologies involving microbes are required for their zero negative impact on the environment. One such microbe applied was *Desulfobibrio desulfuricans* for palladium recovery from aqueous solution and electronic wastes (Creamer et al. 2006). *B. thuringiensis* Y9 could reduce Pd²⁺ at 93 mg/g and 60 mg/g efficiency in the absence and presence of O₂ to PdNPs at around 99.18 % recovery (Chen et al. 2022). *E. coli* could modify waste Pd-based catalysts to recover approximately 99% of PdNPs. They may carry out Cr(VI) removal at around five recycles (Yu et al. 2023). However, work on recycling and recovery of PdNPs is still at its naïve; hence, research must be conducted on it. Regulatory and ethical issues during the recovery of nanoparticles and their application in biomedicine are mainly concerned with the health risk to workers handling them. To date, the main scientific explanation regarding environmental application remains unknown.

CONCLUSION AND FUTURE TARGETS

In recent years, nanotechnology has developed immensely because of its wide implications in various fields of science and technology. Alternative biological methods, compared to the physico-chemical approach, have several advantages, like being eco-friendly, simple, and lucrative. Thus, the sustainable production of these nanoscale components utilizing biotic assets has immense prospects, like stable, controlled size and shape nanomaterials. In the present review, we have delivered an overview of the biological production of PdNPs by employing numerous microbes as well as chemical extracts derived from unicellular and multicellular plants. The intrusion of biogenic formation of PdNPs over physicochemical methods

is preferable as it's ecologically benign, less charged, along uncomplicated character. In addition, various biological products like exopolysaccharides may be useful together as reducers and stabilizers for palladium nanoparticle formulation in the single-pot method.

The biological approach for nanopalladium material formation encompasses a widespread choice of sources like plants, bacteria, and actinomycetes. Reports are still rare on the implications of yeast and fungi regarding the biological production of PdNPs. Nowadays, the exploration of the formation of bioPdNPs is still in the innovative phase. Thus, as a prospect, (i) researchers should try to find out the answer to some questions that are still unanswered. (ii) Investigations are further required in the future to find out the optimized factors to apprehend the influence of varied process parameters during the development of PdNPs. (iii) Continuous attempts should be made to emphasize the mode of PdNPs synthesis and the effect of its structural properties for its diverse applications. Moreover, an inspection of former reports suggests the synthesis of palladium nanoparticles on a small scale. To date, no single report has focused on the large-scale production of PdNPs exhausting biological sources. Therefore, (iv) developing palladium nanoparticles by exploring biological sources at an industrial scale can be of great interest to researchers. Thus, it can be considered the best platform for researchers to propose a safer scheme for developing nanoparticles for better perception and knowledge towards green and sustainable approaches.

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