

Review Paper

A Compendium On The Eco-Sustainable Biosynthesis Of PdNps And Its New Avenues Towards Environmental Applications

Geetanjali Basak[†][†]Department of Microbiology, Raniganj Girls' College, Raniganj, West Bengal, IndiaEmail id: geetanjaliBasak@gmail.com/ tgeetanjali_microbiology@raniganjgirlscollege.orgORCID id: <https://orcid.org/0000-0002-0706-191X>

Abstract: PdNps are considered as significant catalytic agents, along with wide range of applications mainly hydrogen storage and sensing, biomedical imaging and remediation strategies. Extensive studies are being carried out on formation of PdNps (PdNps) worldwide, shows the predominancy of 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 the ecosystem. Therefore, the present review provides an over view of the modernized techniques involved in the biological approach for PdNps formation by utilising various natural origin 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 utilised for the characterization of bioPdNps are described with an insight being delivered on the utility of biologically synthesized palladium nanoparticle. Recovery of PdNps to achieve circular economy is also being focused. In addition, the future prospectus on palladium nanoparticle research is also summarized.

Key Words	BioPdNps; Biosynthesis; Environmental remediation; Microorganism; Properties
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1. INTRODUCTION

Palladium is considered as one of the most extensively utilised gracious, switching metal that displays typical physico-chemical, optical and thermodynamic characteristics at nanoscale margin (Watanabe et al. 2006, Cheong et al. 2010). Although the metal palladium was the interest of the researcher from ancient times, its revitalization as PdNps have resulted to 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 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 as good catalyst in both homogeneous and heterogeneous reactions as it owes enhanced surface-to-volume ratio with great surface energy (Narayanan & Sayed 2005). Moreover, PdNps performs a vital part in several biotechnological fields such as production of pharmaceutical compounds, degradation of harmful environmental pollutants (Kora & Rastogi 2016, Martins et al. 2016, Safavi & Momeni 2012) and preparation of non-enzymatic biosensor to detect hydrogen peroxide in milk (Baccar et al. 2013).

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. Top 5 competitive regions that are involved in its manufacture and applications are North America, Europe, Asia Pacific, Latin America and Middle East & Africa, as data provided by 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 catalyst in the automobile sector. They also act as catalysts for degrading hydrocarbons in petroleum site. U.S plays the dominant role succeeded by Germany and U.K. North America and Europe contributes about 45% of market share descended by China and Japan around 30 %. Finally Latin America and Middle East & Africa follows the path by counting around 15 % of market share and remaining contributed by Brazil and Saudi Arabia.

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 uniform sized palladium colloidal particles have been considered as an essential matter in research. Several approaches, particularly uniform shaped palladium particles in aqueous solutions by wide variety of stabilizing agents have been used by the researchers (Ganesan et al. 2007). Fig.1 shows the traditional methods for materializing of PdNps.

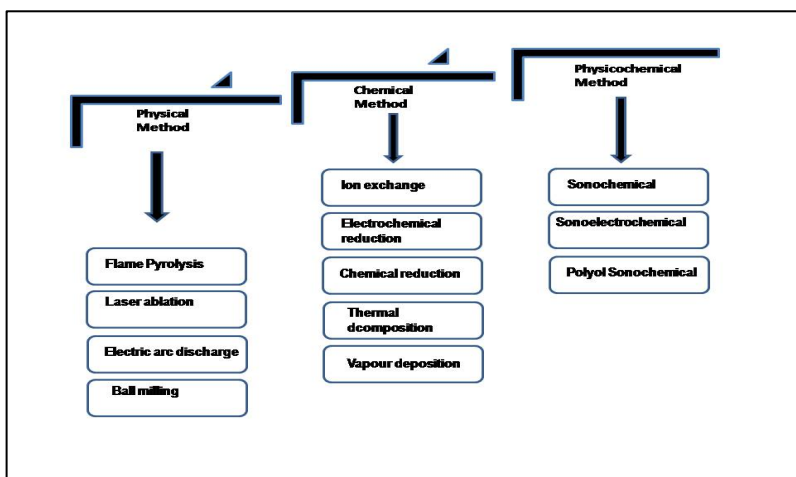


Fig.1: Traditional methods for materializing of PdNps.

Among various techniques, 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 risk to the environment and health of living beings. Hence, there is an increasing demand aimed at the development of clean, nontoxic and ecological synthetic approach. The expansion of enhanced production and inexpensive technology for nanoparticles creation is a crucial task. Till date, enormous variety of microorganisms, involving prokaryotes and eukaryotes, had been accounted for the the formation of nanobiomaterials (Basak et al. 2014, Basak et al. 2020). Although reports are there on its biosynthesis and applications, still reports are scanty on its mechanism of synthesis through microbes and ‘RRR’ concept. The author has tried to portray these informations about PdNps from its cradle to grave. Probably, this is the first report to through a compendium including the aforementioned aspects, challenges and benefits as environmental clean up as well.

Therefore, the current study envisage on the overall technology applied for the sustainable preparation of PdNps throughout the last decade. The objective of the refurbished report is also to conjugate various literature about PdNps utilities in several fields involved in environmental applications. Moreover, the review tries to envisage future prospects, challenges and research facilities regarding the particular area of interest. Furthermore, the recovery, recycle, reuse (‘RRR’) is also being discussed in the particular comprehensive review.

2. METHODOLOGY

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

3. BIOSYNTHESIS OF PdNps

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

3.1. Biological Formation of nano-palladium by Using Plant Extracts

Biological process involving plant extract is found to be uncomplicated and adaptable technique followed during the formation of PdNps (Fig. 2).

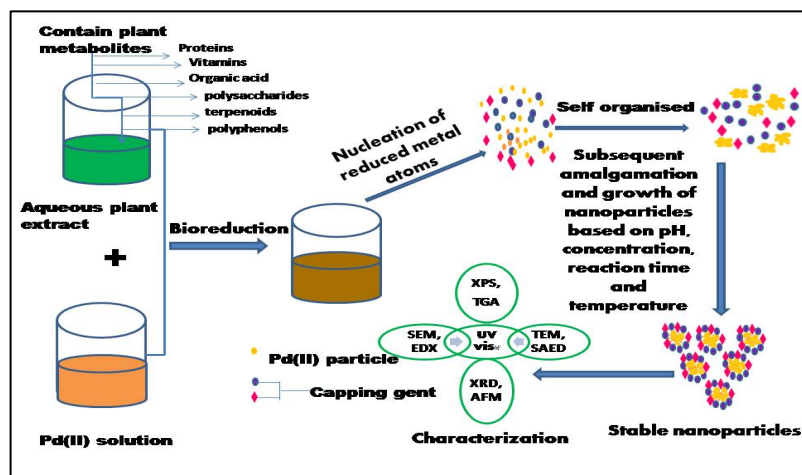


Fig. 2: General route for the biological formulation of nano-biopalladium through plant metabolites

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

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 camphora</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 Xyedoensis</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	

For the biosynthesis of nano palladium, the chosen extract of plant will be mixed with palladium salt solution at a specified concentration under ambient condition in a single step experiment (Fig. 2). In 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 reduction of metal salt to a visual colour alteration. The phytochemicals/metabolites extracted from various plants used for PdNps formation are polyols, polyphenols, flavonoids, vitamins, organic acid, polysaccharides, terpenoids and proteins. This particular plant extracts are reported to biogenically synthesize nanosized Palladium particles (Qazi et al. 2016).

3.2. Microbe Mediated Synthesis of nano-palladium Particles

Nano sized palladium particles formed by microbial factories has come out as a promising complementary method that demands to achieve environmental sustainability with enhanced strength and controlled morphology of nanoparticles (Shedbalkar et al. 2014). Several experiments using various bacteria (a palladium compatible agent) were being 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 by two ways *viz.* (i) intracellular mode of action and (ii) extracellular mode of action (as shown in Fig. 3).

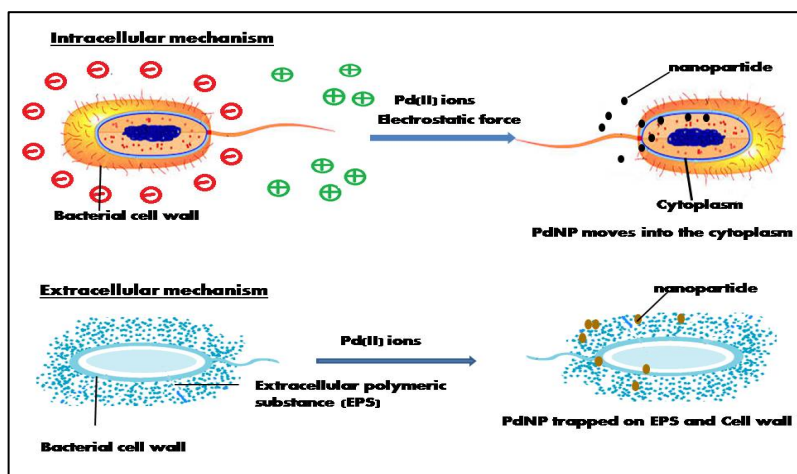


Fig. 3: Mode of action involved in the microbe mediated nano-palladium particle formation

3.2.1. 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 are reports on bacteria (*B. benzeovorans* NCIMB 12555, *D. desulfuricans* NCIMB 8307 and *D. desulfuricans* NCIMB 8326) for 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, till date information about the formation of intracellular palladium are very limited for eg. intracellular palladium situated within the inner membrane (Foulkes et al. 2011). Although

microbes act as biogenic bearer of Palladium whose valency is converted from 2^+ to 0, they lose their viability but still *E. coli* could remain physiologically activated with inability to proliferate (Joudeh et al. 2021).

3.2.2. Extracellular Mode

Here the palladium colloidal suspension are present over the outer wall of periplasm, plasmalemma or surface of the cellwall, especially on the extracellular polymeric substance can be observed. Several reports have been conveyed on the use of 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 of the oxidation phase from +2 to 0 of PdNps lying over periphery on the cell. Thus it makes the metallic ion non toxic, along with suitable retrieval of nanoparticle without cell destruction. The basic mechanism for extracellular formation of PdNps is through microbial hydrogenase enzyme (Yang et al. 2020). Formation of bionano-palladium particles by members belonging to the groups of fungi (Tarver et al. 2019) are being reported so far. Few algae viz. *Chlorella vulgaris* (Arsiya et al. 2017) and *P.boryanum* UTEX 485 (Maggy et al. 2007) are being accounted for making nano-palladium particles. Table 2 shows collection of microbes for PdNp formation.

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

Plectonema boryanum ≤ 30 nm, spherical and Maggy et al. 2007
elongated

3.3. PdNps Synthesis through Biological Products

Apart from microbial synthesis of PdNps, usage of secondary metabolites regarding development of PdNps, gives budget friendly solutions for attainment of safer earth. Among biomolecules, nucleic acids such as RNA serves as great biogenic catalysts for 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 H₂O₂ and oxidizing capacity of ascorbic acid (Fang et al. 2007).

The utilization of high molecular weighted biomolecules viz. protein, polypeptide and amino acid varied sequence for stabilization of peptide chains have been reported to ensure a substantial influence over nanomaterial structure. An amino acid residue can perform dual role in increasing the stability alongwith reduction simultaneously. Zhou et al. (2016) showed the potential of biofilm producing natural polymer externally bear 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 are carried on top of the outer layer of concave-fiber membranes so as to carry (H₂) for electron donation. Several exopolysaccharides like xanthan gum, obtained by fermentation of bacterium *Xanthomonas campestris* acts both as 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 acid (Ameri et al. 2020) and oxytocin + amino acid (Bendre et al. 2020) act as potential agents for synthesis of the target material recently. Clergeaud et al. (2013) depicted that lipid, glycerol monooleate along with tetrachloropalladate solution synthesized 4 nm sized PdNps. This is mainly accompanied by polyol-type reaction where the palladium is formed from reduction of palladium through a hydroxyl group present in glycerol at 25° C.

3.4. Significant Parameters for PdNps Synthesis

Important parameters considered for regulated synthesis of PdNps are as follows (i) pH, (ii) the type and amount of the stabilising 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 optimised 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 caps on the same shaped palladium nuclei. The precursor PdCl₂ was reacted with ethane 1,2 diol at 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 atmosphere alongwith 6.3 nm sized particles

in 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 found to play a crucial role. A higher reductant concentration might result in an enhanced reduction rate of change in morphology of nanomaterials (Xiong et al. 2007). Size of the nano-palladium can be transformed based on the different preliminary concentration of PdCl₂ over amine. Reaction temperature is one of the main factors that not only affects the reduction rate of metal precursor, but in addition bring about morphological change in Palladium nanomaterials. Guisbier et al. (2011) explained about the consequences of various temperatures triggering changes in the geometrical shape of PdNps. Several works have emphasized about the influence of foreign species (trace metallic ions) on control 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.

3.5. Properties and Characterization of BioPalladium nanomaterials

3.5.1. Properties

PdNps owe interesting properties compared to the metal ion itself, that contributes for immense medicinal application. 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 to find out novel approach for PdNps synthesis with improved properties. Due to their catalytic and/or optical properties, they had several environmental applications that will be discussed in the review. Though PdNps impart excellent mechanical and chemical stability, but still they are 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, and are being reported to reduce and stabilize PdNps (Coockson, 2012). Electrostatic force of attraction or a combination of the two i.e. oppositely charged forces might be the reason for stabilization.

3.5.2. Characterization

Biologically synthesized PdNps can be observed through various instrumentation techniques. A series of analytical techniques must be accompanied to determine the character of the material. Starting with the colloidal suspension, colour change of the synthetic solution to brownish back from orange confirm the formation of PdNps. These biopalladium nanomaterials are initially detected by UV-vis spectrophotometer. FT-IR spectral analysis is being used in various biological agents to spot out the charged groups occurring over the superficial of material required for addition of the 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 its bulk version (crystal). A detailed diffraction study illustrates the most significant peak instigated because of crystal the crystal unit cell structure of PdNps. The elements present and characterization of a nanoparticle is being analysed using the instrumentation technique of energy dispersive X ray (Omajali et al. 2015). Both elemental

analysis and surface characterization can be analysed by X ray photoelectron spectral (XPS) techniques. Difference in kinetic energy from similar dispersed state of the particle size, derived at varying magnitude of experiments in between different core levels determines the morphology of particles. Optionally, the average size of the particle can also be analyzed from fraction of monolayer and crystallite samples on concentration basis. In case of formation of nanoparticles located intracellularly, the dimension of the nanoparticle is very minimum. This can be voluntarily visualized in Transmission electron microscopy. Therefore, it is necessary to analyze electron back scattering and confirmatory analysis via EDX analysis. In addition, it may also show 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 biosynthesis of PdNps through EDX analysis (Tahir et al. 2016). Identification of palladium, phosphorous and sulfur within *D. desulfuricans* and *B. benzeovorans* cells was illustrated by EDX (Omajali et al. 2015). Further existence of these particular elements were established by Scanning transmission electron microscopy (STEM) that visibly revealed the entrapped miniature sized particle 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 their organization depending on its functionality is determined by SEM. The crystalline structure and size of PdNps is further investigated through high resolution TEM (HRTEM) - selected area electron diffraction (SAED). A schematic diagram presenting the factors, properties and characterization of PdNps is being highlighted in fig. 4.

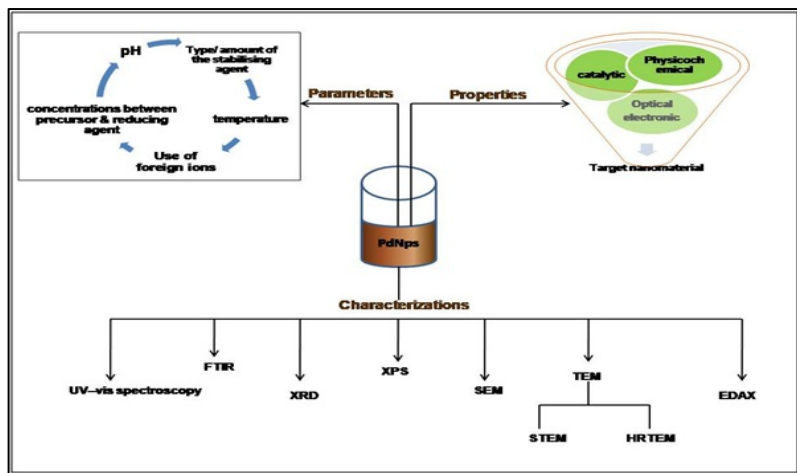


Fig. 4: Properties and instrumental analysis of nano-palladium particle

3.6. Environmental Applications Of PdNps

Rapid expansion of concentration of the contaminants released through the commercialized world pose a threat to the living beings. Hence the researchers are trying to combat these problems by several modern attempts like use of any external stabilizing agents is not required as various biological constituents extracted from floras and microorganisms can solely act 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.

3.6.1 Removal of Dyes

Enhanced modernization and industrial activity have generated the discharge of dyes that hazardous effect on the ecological balance on 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 enhanced photocatalytic role in degrading phenol red dye at an optimized pH 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 and 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. 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 significant enhanced removal of over 99% through sodium borohydride within reaction mixture. Simultaneously, the nanoparticle could be detached from the synthetic solution in existence of the magnetic field applied externally. These nanobiomaterials can be reutilised again after being repeated cycling of nine times without any potential effect in its catalytic activity. Therefore, these qualities enabled this catalyst to be an encouraging contestant in the arena of energy and environment (Li et al., 2015).

3.6.2. Removal of Nitrophenol

Nitrophenols are one among various contaminants that leads to cancer and must be reduced to aminophenols. Experiment have been conducted by using *Phoenix dactylifera* synthesized PdNps for degradation of 4-nitrophenol to 4-aminophenol in existence of catalyst within 2 min thereby forming 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 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 minimum quantity. The particle also owed efficient catalytic property 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 biocompatible polymer named gum olibanum obtained from *B. serrata*. This bifunctional agent reduce and stabilize the nanomaterial simultaneously. Spherical sized nanoparticle ranging from 2.5–8.8 nm were resistant to bacteria of different cell wall still at their 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).

3.6.3. Removal of Pesticides and Heavy Metals

Pesticides are one such pollutants that upon being discharged into the effluent or solid waste, cause harm to human health. Biosynthesized Palladium nano sized particles effectively degrade dehalogenates PCBs (Windt et al. 2005); perchlorate and nitrate (De Windt et al. 2006), and PBDEs (Harrad et al. 2007, Deplanche et al. 2009), trichloroethylene (TCE) (Hennebel et al. 2009), lindane and chlorobenzenes (Mertens et al. 2007) and diatrazin (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. Productively formation of ferric oxide conjugated palladium nanobiparticles could eliminate Hexavalent chromium to trivalent chromium in synthetic liquid environment in presence of formic acid (Kalantari et al. 2021).

3.6.4. Removal of Antibiotics

Essential pharmaceutical components like antibiotics are being utilized by patients at around 30 %, rest remain deposited in wastewater or sludge due to the human's excretory activities. Thus it is important to take necessary steps reduced dispense and aggregation of relentless antibiotics into the ecosystem (Gavrilescu et al. 2015). Ciprofloxacin is one such antibiotic that induce mutation as well as cancer, have been eliminated in incidence of hydrogen. The ciprofloxacin and hydrogenated palladium ion conjugates is 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 presence of microbes *Desulfovibrio vulgaris* synthesized PdNps because of sulfamethoxazole (Martins et al. 2017).

3.7.Challenges

BioPdNps definitely dominates 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 surface (Matsena and Chirwa 2021). Crucial parameters viz. localization, morphology of nanoparticles depends on microbial species. Biomolecules are involved in process hence nanomaterials may be of different sizes (Filice et al. 2021). It may have an adverse impact on seed germination and get accumulated in living organisms of the environment (Xiaodi et al. 2024). With increase in use of PdNps for controlling automobile exhaust pollutants, imbalance in

biogeochemical cycles may occur. So risk analysis of palladium are crucial to regulate their utility as catalytic converter to obtain a sustainable earth (Arzoo et al. 2022).

3.8. Recovery Of The Palladium Towards The Achievement Of Circular Economy

Economic upliftment requires commercialization that consequents to pollution of the ecological system because of the dispense of toxic metals. Hence technologies must be there to recover, recycle and reuse them especially certain heavy metals viz. Au, Ag, Pd etc. that are precious in terms of cost and its various applications as catalyst hydrogenation, oxidation, and dichlorination, gas sensing and hydrogen storage (Klinkova et al. 2017). Moreover ecofriendly processes must be applied to recover high rate (~99.0 %) and purity of palladium through union of copper capture and electrodeposition technique in presence of 0.5 molar nitric acid that had no adverse effect on the earth (Liu et al. 2020). Speedy, cheap and ecosustainable methods are to be involved for recycling, recovery of the PdNps so that they can be reused for example pulsed laser ablation process is a powerful and energetic process that could isolate nanoparticles within 30 mins of its irradiation (Lee et al. 2021). Recently microbes are used in the formulation of nanoparticles. Although heavy metal hazards affects the microbial life, still they can combat by diffusing the toxicity of metals through their actions at gene and protein level (Veisi et al 2016, Patel et al. 2021, Law et al. 2022). Economically profitable and sustainable technologies involving microbes are required for its zero negative impact on 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 Pd^{2+} at 93 mg/g and 60 mg/g efficiency in absence and presence of O_2 to PdNps at around 99.18 % recovery (Chen et al. 2022). *E. coli* could modify waste Pd based catalyst 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 are still at its naïve hence research must be conducted on it. Regulatory and ethical issues during recovery of nanoparticles, its application in biomedicine is mainly concerned with the health risk of workers handling it. Till date the main scientific explanation regarding environmental application remains unknown.

4. CONCLUSION AND FUTURE TARGETS

In the recent years, nanotechnology is developing immensely because of its wide implications in various fields of science and technology. Alternative biological methods compared to physico-chemical approach owes several advantages like being eco-friendly, simple and lucrative. Thus, the sustainable production of these nanoscale components utilising biotic assets have immense prospects like stable controlled size and shaped nanomaterials. In the present review, we have delivered an overview on the biological production of PdNps by employing numerous microbes as well as chemical extracts derived from unicellular and multicellular plant. The intrusion of biogenic formation of PdNps over physicochemical methods is preferable as it's ecologically benign, less charged along with uncomplicated character. In addition, various biological products like exopolysaccharides may be useful together as reducer and stabilizer for palladium nanoparticle formulation in single-pot method.

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

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