IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 15, Issue 6 Ser. II (June 2022), PP 30-36
www.iosrjournals.org

Green Synthesis of Palladium (Pd) Nanomaterials using Plant Extracts for Catalysis and Biological Applications

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Abstract:
Here in we discussed the biogenic synthesis of palladium (Pd) nanomaterials from plants and microbes because it is cost-effective, sustainable, and environmentally friendly. Plants and their parts are known to contain a variety of primary and secondary metabolites that convert metal salts to metal nanoparticles. The pH, temperature, incubation time, and concentrations of plant extract and metal salt all have an effect on the shape, size, and stability of Pd nanoparticles. Pd nanoparticles are widely used in catalysis, drug delivery, and cancer treatment. They have demonstrated size and shape-dependent specificity and selectivity in therapeutic properties. We discussed the biogenic fabrication of Pd nanoparticles, their potential applications as catalysts, medicine, and biosensors in this review.

Key words: *Biogenic synthesis, herbal extract, phytochemicals, metal nanoparticles, cancer treatment.*

Date of Submission: 14-06-2022 Date of Acceptance: 29-06-2022

I. Introduction

The primary goal of green synthesis is to reduce the use of toxic chemicals in order to protect the environment from pollution. As a result, biogenic routes for nanomaterial fabrication are becoming increasingly popular. The three main conditions for the preparation of nanomaterials are (i) The use of an environmentally friendly solvent medium, (ii) a reducing agent, and (iii) a nontoxic material for their stabilisation. Nanomaterials derived from plants, fungi, and bacteria have a wide range of potential applications in science and technology [1–10]. Metal ions are reduced by proteins, amines, amino acids, phenols, sugars, ketones, aldehydes, and carboxylic acids found in plants and microbes. The geometrical shape, size, and stability of nanoparticles can be controlled by monitoring the p^H, temperature, incubation time, and plant extract and metal salt concentrations. Both palladium and silvery white precious metals have a high density. The biogenic fabrication of palladium nanoparticles has used *Anogeissus latifolia, Cinnamom zeylanicum, Cinnamomum camphora, Curcuma longa, Doipyros kaki, Gardenia jasminoides, Glycine max, Musa paradisica, Ocimun sanctum, Pinus resinosa,* and *Pulicaria glutinosa*. Because of their high surface energy and large surface-to-volume ratio, palladium and platinum nanoparticles synthesised from various plant parts are used as both heterogeneous and homogeneous catalysts [11]. They are used in a variety of medical diagnostic procedures without causing Damage to DNA [12].

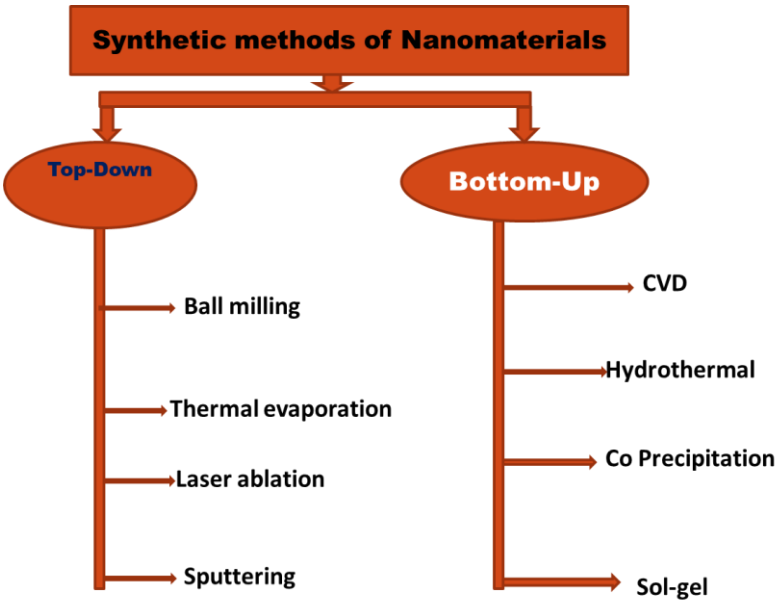

Figure 1: Synthesis of nanomaterial Approaches.

In the Suzuki–Miyaura coupling reaction, palladium nanoparticles derived from herbal extracts were tested for heterogeneous catalytic activity [13]. It can be performed in an aqueous medium without fear of dissociation because it is a ligand-free catalytic reaction. Under normal conditions, even with one mole palladium nanoparticles, the yield is very high. In this review, we talked about the biosynthesis and characterization of palladium nanoparticles using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-Vis, and Fourier transform infrared (FTIR) spectroscopy. Their potential applications in catalysis, cancer treatment, and other biological sciences have also been researched.

Palladium Nanoparticle Biosynthesis.

When an aqueous solution of $[Pd(OAc)_2]$ was stirred with a methanolic extract of *Catharanthus roseus* for 1 hour at 60°C, the color changed. It had a UV-visible absorption peak between 360 and 400 nm, corresponding to 40 nm spherical palladium nanoparticles. *C. roseus* extract is a mixture of eight compounds containing –OH groups, which reduce metal ions to metal nanoparticles. The synthesis, characterization, and application of palladium nanoparticles as a photocatalyst agent have all been reported [14, 15]. Palladium nanoparticles were used to investigate the degradation of phenol red. At room temperature and at different pH levels (2–10), the nanoparticles were mixed with phenol red. The surface plasmon resonance (SPR) band of the dye at 433 nm disappeared at pH 6, indicating phenol red degradation [15].

Table 1: Size and shapes of Pd nanomaterials

Plant Sources	Part used	Nanoparticles	Size (nm)	Shape	References
Anogeissus latifolia	Gum	Pd	4.8	Spherical	[39]
Azadirachta indica	Leaves	pd	5–50	Small and large spheres	[62]
Cinnamom zeylanicum	Bark	Pd	15–20	Crystalline	[23]
Cinnamomum camphora	Leaves	Pd	3.2–6.0	–	[86]
Curcuma longa	Tuber	Pd	10–15	Spherical	[26]
Doipyros kaki	Leaves	Pd	2–12	Crystalline	[26]
Euphorbia granulate	Leaves	Pd	25–35	–	[44]
Gardenia jasminoides	Leaves	Pd	3–5	–	[27]
Glycine max	Leaves	Pd	15	Spherical	[34]
Moringa oleifera	Waste petal	Pd	10–50	Spherical	[42]
Moringa oleifera	Peel extract	Pd	27 ± 2	Spherical	[43]
Musa paradisica	Peeled banana	Pd	50	Crystalline irregular	[33]
Ocimun sanctum	Leaves	Pd	23	Irregular	[55]
Pulicaria glutinosa	Whole plant	Pd	20–25	Crystalline and spherical	[35]
Pinus resinosa	Bark	Pd	16–20	Crystalline	[58]
Pinus resinosa	Bark	Pd	6–8	Irregular	[45]

Prunus* x *yedoensis	**Leaves**	**Pd**	**50–150**	**Spherical**	**[45]**

Palladium nanoparticles derived from aqueous leaf extract of *Hippophae rhamnoides* have been reported [13]. They were characterised using SEM, TEM, XRD, UV-Vis, and FTIR spectroscopy. Polyphenols were found to function as reducing and capping agents for palladium nanoparticles. Particle sizes ranged from 2.5 to 14 nm, with the vast majority being spherical. Their catalytic activity as a heterogeneous catalyst for the Suzuki–Miyaura coupling reaction in water was investigated under lignin-free conditions. The reaction of iodobenzene with phenylboronic acid in the presence of palladium nanoparticles at 100 °C in alkaline medium yielded a 100% product yield. When numerous aryl halides were combined with phenyl-boronic acid, they all produced the corresponding compounds in high yield (91–95%). Momeni and Nabipour [16] created palladium nanoparticles using the *Sargassum bovinum alga*. Using UV-Vis spectroscopy in the 300–800 nm range, the authors observed the conversion of palladium ions into metallic palladium. A change in colour from yellow to dark brown indicated the formation of palladium nanoparticles. Bimetallic nanoparticles with core-shell structure and shape-controlled synthesis have been reported for Au@Pd nanoparticles [17, 18]. Another metal was added to a reduced gold nanoparticle before it was chemically reduced or reduced with a plant extract containing a mild reducing agent (*Cacumen platycladi* leaf extract). The gold nanoparticles were encased by the second metal nanoparticles, resulting in a specific shape determined by how the second metal nanoparticles were arranged around the gold. Because Pd and Fe are magnetic, they were recovered from the reaction mixture with a magnet and reused with negligible activity loss for Sonogashira coupling reactions. Palladium nanoparticles were biosynthesised on reduced graphene oxide using barberry fruit extract and used as a heterogeneous catalyst in a 1:2 alcohol–water mixture at 50 °C [21]. Because vitamin C appears to be the most plentiful phytochemical in the extract, it appears to have reduced the metal ions to nanoparticles. Palladium nanoparticles were discovered to have an average size of nearly 18 nm. By reducing nitrobenzene to aniline, the catalytic activity of $NaBH_4$ was determined.

The reduction takes place on the catalyst's surface and is determined by the rate of nitro compound absorption on the catalyst's active site. The procedure is complex, but it is done in stages. Adsorption of H_2 and nitro compounds occurs, followed by electron transfer from the BH unit to the nitro derivative, and finally, amino compound desorption from the catalyst's surface. The catalyst can be used five times without significantly losing activity.

Salvadora persica root extract was recently used to create palladium nanoparticles. The extract contained polyphenols, which acted as both a bio-reductant and a stabilising agent [22]. Average nanoparticles of 10 nm were obtained at 90 °C, as determined by the loss of color and disappearance of an absorption band at 415 nm in the UV-Vis spectrum of the colloidal solution. Palladium nanoparticles were produced at 30 °C by combining C. zeylanicum bark extract and $PdCl_2$ [23]. Although the reaction began after 24 hours, it took 72 hours to complete. The nanoparticles were polydispersed and spherical in shape, measuring 15 to 20 nm in size. Increasing concentrations of leaf extract influenced their formation. The XRD pattern confirmed the existence of crystallization palladium. Although pH has had no effect on nanoparticle formation, precipitation occurs above pH 6. It has no effect on the shape of nanoparticles, but it does have a minor effect on their size [24]. At 30 °C, a 5-ml extract was treated with 50 ml of 1 mM $PdCl_2$ and nearly 60% of the $PdCl_2$ was reduced to palladium nanoparticles. Higher biomaterial concentrations could reduce the remaining 40% $PdCl_2$; otherwise, the suspension would contain both the Pd^{2+} ions and the palladium nanoparticles. Linalool, eugenol, methyl chavicol, cinnamaldehyde, ethyl cinnamate, and caryophyllene [25] have indeed been found in C. zeylanicum bark extract and have been shown to convert Pd ions to Pd nanoparticles. However, no clear mechanism has been proposed for the reduction of $PdCl_2$ to Pd nanoparticles. Sathish kumar et al. [26] biosynthesised palladium nanoparticles from *C. longa* extract. The 10–15 nm nanoparticles are thought to be formed through a redox process in which polyphenols act as a reducing agent. They were found to be stable even after three months. The pH of the solution had almost no effect on nanoparticle formation, but size increased as pH increased. Green synthesis of palladium nanoparticles from dried fruit extract of *G. jasminoides* Ellis was achieved after 1.5 hours of incubation at 60 °C [27]. A color shift from orange to dark brown indicated the formation of nanoparticles. Three distinct absorption peaks were observed in the extract at 238, 322, and 440 nm, which corresponded to geniposide [28], chlorogenic acid [29], and caffeine [30]. Palladium nanoparticles were biogenically synthesized from biodegradable banana peel extract and defined using UV-Vis, IR, SEM, and XRD [33]. The peel extract powder reacted with $PdCl_2$ in water for 3 minutes at 80 °C. The UV-Vis spectra of all mixtures showed a 400 nm peak, but when Pd^{2+} was reduced to Pd (0), the peaks shifted or disappeared, with a constant change in colour from yellow to red due to surface plasmon vibration excitation in the palladium nanoparticle. The SEM images revealed nanoparticles and aggregates. Dendrites form as a result of accumulation and resemble a lovely flower twig. Dendrites, on the other hand, are revealed to be made up of micro cubes that are neatly arranged as a motif at higher magnification. The average size of palladium nanomaterials was 50 nm. The presence of carboxyl, amino, and hydroxyl groups was revealed by the FTIR spectral data, which are thought to be active ingredients in $PdCl_2$ reduction.

Petla et al. [34] created palladium nanoparticles from soybean leaf extract (G. max). Despite the fact that the reduction began after 5 minutes, the characteristic absorption peak for Pd^{2+} at 420 nm vanished completely after 48 hours, indicating that Pd^{2+} was completely converted to Pd (0). The TEM micrograph revealed the formation of uniform spherical particles 15 nm in size. Palladium nanoparticles were biosynthesized from *P. glutinosa* plant extract at 90 °C after stirring the mixture of $PdCl_2$ extract for 2 hours [35]. A change in colour from light yellow to dark brown, as confirmed by UV-Vis spectral analysis, indicated the formation of palladium nanoparticles. A TEM micrograph revealed palladium nanoparticles with diameters of 20–25 nm that were capped and reduced by an organic layer derived from the extract. The IR spectrum of the plant revealed the presence of flavonoids and polyphenols. Their catalytic activity was investigated in the Suzuki reaction of bromobenzene with phenylboronic acid in an aqueous medium without prior activation [36] under anaerobic conditions in the presence of SDS and K_3PO_4. Biphenyl was obtained when only 5% of palladium nanoparticles were used as a catalyst. The response was quick and effective, with nearly 60% conversion achieved in the first 1 minute and completed in 4 minutes. Recently, palladium nanoparticles were created using Arabidopsis plant culture and K_2PdCl_4 [38]. The reduction took only 24 hours to complete. During the first three hours, TEM images of various plant sections revealed well-dispersed spherical metallic nanoparticles with an average diameter of 3 nm. As the incubation time increased, the size and concentration of nanoparticles increased up to 32 nm. They were evenly distributed throughout the apoplast regions. The plant had reached its maximum palladium concentration after 24 hours. The mechanism of Pd^{2+} ion reduction to elemental Pd within the plant system is still unknown. However, prior to the formation of nanoparticles, one of the likely steps is the binding of Pd^{2+} ions to carboxyl, amino, and sulfhydryl groups present in the plant. A chemical-based reduction process was performed in an isolated system using a single chemical, whereas biological reductions occur in the presence of biomolecules in a biological system such as plants or microbes.

Aside from biosynthesis, Kora and Rastogi [39] investigated palladium nanoparticles' properties as an antioxidant and a catalyst. Gum ghatti (*A. latifolia*), a water soluble plant gum polymer, was allowed to react with $PdCl_2$ for 30 minutes at 121 °C and 103 K Pa, resulting in a change in colour and the disappearance of an absorption peak at 427 nm in the UV-Vis region. The nanoparticles were spherical in shape and poly-dispersed, with an average size of 46 nm. The hydroxyl and carboxyl groups of the gum are thought to be first bonded to Pd^{2+} ions, which then reduce and stabilise them. The proteins and polysaccharides in the gum are thought to stabilise and cap the nanoparticles. Palladium nanoparticles were created using *Moringa oleifera* biomass and bis-phthalate as a natural reducing and capping agent. Their average size ranged between 10 and 50 nm. They were spherical, distributed evenly, and did not aggregate [42]. The phytochemicals reduced the size of the palladium nanoparticles, according to TEM analysis. *M. oleifera* peel extract has also been used for palladium nanoparticle fabrication [43], as evidenced by the Zeta potential and GC-MS, as well as UV-Vis spectroscopy, XRD, SEM, and HR-TEM analyses. At room temperature, palladium nanoparticles derived from *Euphorbia granulate* leaf extract were used as a heterogeneous catalyst in the phosphine-free Suzuki–Miyaura coupling reaction [44]. According to a TEM micrograph, the palladium nanoparticles were 25–35 nm in size.

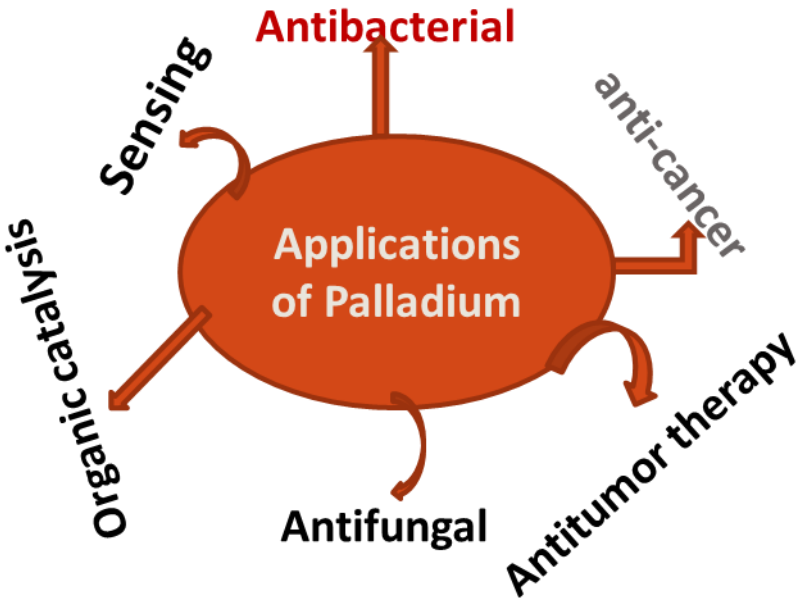

Figure 2: Applications of Palladium (Pd) nanomaterial

Palladium nanoparticles were made from *Prunus yedoensis* leaf extract and then characterized using UV-Vis, XRD, FTIR, HR-TEM, and SAED [45].
The formation of palladium nanoparticles was confirmed by a colour change from light yellow to dark brown. For the production of palladium nanoparticles, Manikandan et al. [45] proposed pH 7, 3 mM Pd(II), and a 30-min incubation time (table 1 shows shape and size of Pd nanomaterials).

Application of Palladium Nanoparticles

As a glucose biosensor, palladium nanoparticles doped with chitosan–graphene have been used [36]. Palladium nanoparticles on graphene oxide were also used as a recyclable heterogeneous catalyst for the reduction of nitroarenes with sodium borohydride. Because the recovered catalyst can be used for five cycles, it can be used on a large scale to reduce nitroarenes. It has also been used in the production of methylene blue, methyl orange, and nitro phenol. Because the nanoparticles degraded the above dyes so well, they can be used to treat affluent containing dyes. Palladium and platinum are both commonly used in the oxidative addition and reductive elimination of hydrogen. Platinum-treated asbestos is used in many catalytic [49] reactions. For example, (i) in the contact process to produce H_2SO_4, (ii) in the Ostwald process to convert NH_3 to NO to produce HNO_3, (iii) methyl to formaldehyde oxidation, and (iv)Hydrazine decomposition to nitrogen and ammonia. Platinum-gold dendrimer-like nanoparticles supported on polydopamine graphene oxide reduce nitrophenol to aminophenol [50]. The ability to catalyse the reduction is determined by the platinum-gold ratio. Palladium nanoparticles were synthesised from *S. persica* root extract, and their catalytic activity in the Suzuki coupling reactions of aryl halides with benze- neboronic acid in water to biphenyl was investigated [22]. Although the major conversion occurred in the first 2 minutes, the efficiency of the conversion rate as a function of time and yield follows the order iodobenzene > bromobenzene > chlorobenzene. The palladium nanoparticles used as a catalyst can only be reused three times (figure 2). Another study used *Myrtus communis* leaf extract to produce Pd/TiO_2 nanoparticles [51]. The authors demonstrated that Pd/ TiO_2 nanoparticles, which are highly efficient, stable, and recyclable, could be recycled five times without agglomeration. Palladium nanoparticles were synthesised from dried fruit extract of *G. jasminoides* Ellis and measured for catalytic activity by hydrogenating p-nitrotoluene to p-toluidine and then to p-methyl-cyclohexylamine [27]. It is worth noting that while p-toluidine conversion was 100 percent, second reduction was only 26 percent at 80–90 °C. The O. sanctum leaf extract contains palladium, ascorbic acid, and terpenoids, which act as reducing and stabilizing agents. The average particle size was measured at 23 nm. The energy dispersive absorption X-ray spectroscopy (EDAX) revealed a net 71 percent content, whereas the XRD revealed the presence of PtO_2, $K_2(PtCl_4)$, Pt, and $PtCl_2$. One-pot synthesis of platinum and palladium nanoparticles from natural lignin and fulvic in water at pH 7 at 80 °C under aerobic conditions has been reported [58]. These polymers have both reducing and stabilising properties. Palladium nanoparticle formation with $NaBH_4$. After 15 minutes, the nitrophenol absorption peak at 399 nm was reduced, and a new absorption band corresponding to 4-aminophenol appeared at 292 nm.

Platinum nanoparticles were created by combining polyols with polyvinyl pyrrolidone, which stabilized the nanoparticles and prevented them from aggregating. They had diameters of 5–7 and 8–12 nm and shapes of cubic, hexagonal, square, and tetrahedral [59].

The biosynthesis of nanomaterials from *Azadirachta indica* extract was reported by Thirumurugan et al. [62]. TEM analysis revealed the formation of polydispersed nanoparticles ranging in size from small to large spheres (5–50 nm). The rate of fabrication of platinum nanoparticles increased as the reaction temperature increased. The presence of carbonyls, alkanes, and aliphatic amines was indicated by sharp peaks at 1728.22, 1365.60, and 1219.01 cm^{-1}, respectively, in the FTIR spectrum. Terpenoids, which act as a reducing agent as well as a stabilizer for the nanoparticles, were found in *A. indica* leaf broth [60].

II. Conclusions

Under mild conditions, one-pot biogenic synthesis of palladium and platinum nanoparticles from herbal extracts, algae, and fungi is possible. Non-toxic nanoparticles of various shapes and structural motifs (spheres, rods, and rings) can be created and stabilized. Furthermore, they can be optimized by adjusting the pH, temperature, incubation time, and concentrations of plant extract and metal salts. These biogenic nanoparticles can be used as nanomaterials in environmental remediation to scavenge dye from textile industries, as well as in Suzuki coupling reactions for the production of many organic compounds. Antibacterial activity of nanoparticles has also been demonstrated against Gram-negative and Gram-positive bacteria. Platinum group metal complexes are used to treat cancer, but they are toxic to normal cells. It's interesting to note that biogenically synthesized palladium and platinum nanoparticles capped and stabilized by phytochemicals are nontoxic. The functionalized nanoparticles can be used as medicine in treating cancer as well as drug carriers. A new protocol for cancer therapy based on palladium and platinum nanoparticles could be developed, which could be more effective and less toxic than current conventional drugs. Coating them with nontoxic and soluble biopolymers may improve their efficacy.

Authors' contributions:
The authors declare that they have no conflict of interest regarding the publication of this paper.

References

[1]. Zengsheng Han, Le Dong, Jin Zhang, Tianming Cui, Shengfu Chen, Guanglong Ma, Xiaolei Guo and Longgang Wang "Green synthesis of palladium nanoparticles using lentinan for catalytic activity and biological applications" **https://doi.org/10.1039/C9RA08051A**(2019)

[2]. Aruna Jyothi Kora and LoriRastogi" Green synthesis of palladium nanoparticles using gum ghatti (*Anogeissus latifolia*) and its application as an antioxidant and catalyst" https://doi.org/10.1016/j.arabjc.2015.06.024**(2018)**

[3]. Azizi S, Mahdavi Shahri M , Rahman HS , Rahim RA, Rasedee A, Mohamad R "Green synthesis palladium nanoparticles mediated by white tea (*Camellia sinensis*) extract with antioxidant, antibacterial, and antiproliferative activities toward the human leukemia (MOLT-4) cell line" DOI https://doi.org/10.2147/IJN.S149371(2017)**.**

[4]. Kadam. J, Madiwale. S, Bashte. B, Dindorkar. S, Dhawal. P. & More. P." Green mediated synthesis of palladium nanoparticles using aqueous leaf extract of *Gymnema sylvestre* for catalytic reduction of Cr (VI)" *SN AppliedSciences* volume 2, Article number: 1854 **(2020)**

[5]. Sadaf Lebaschi , Malak Hekmati , Hojat Veisi "Green synthesis of palladium nanoparticles mediated by black tea leaves (Camellia sinensis) extract: Catalytic activity in the reduction of 4-nitrophenol and Suzuki-Miyaura coupling reaction under ligand-free conditions" DOI: 10.1016/j.jcis.2016.09.027**(2017)**

[6]. Narasaiah. Palajonna, Kumar Mandal. Badal and Sarada. N C " Green synthesis of Pd NPs from Pimpinella tirupatiensis plant extract and their application in photocatalytic activity dye degradation" Materials Science and Engineering 263 **(2017**) 022013 doi:10.1088/1757-899X/263/2/022013.

[7]. Siddiqi KS, Husen A Fabrication of metal and metal oxide nanoparticles by algae and their toxic effects. Nano Res Lett 11:363**(2016)**

[8]. Fulya Gulbagca,Ayşenur Aygün,Mehmet Gülcan,Sadin Ozdemir,Serpil Gonca,Fatih Şen" Green synthesis of palladium nanoparticles: Preparation, characterization, and investigation of antioxidant, antimicrobial, anticancer, and DNA cleavage activities" https://doi.org/10.1002/aoc.6272(2021)

[9]. Husen A, Siddiqi KS Phytosynthesis of nanoparticles: concept, controversy and application. Nano Res Lett 9:229**(2014)**

[10]. Husen A, Siddiqi KS (2014) Carbon and fullerene nanomaterials in plant system. J Nanobiotechnol 12:16

[11]. Siddiqi KS, Husen A Fabrication of metal nanoparticles from fungi and metal salts: scope and application. Nano Res Lett 11:98**(2016)**

[12]. Siddiqi KS, Husen A Engineered gold nanoparticles and plant adaptation potential. Nano Res Lett 11:400**(2016)**

[13]. Thakkar KN, Mhatre SS, Parikh RY (2010) Biological synthesis of metallic nanoparticles. Nanomedicine 6:257–262

[14]. Nasrollahzadeh M, Sajadi SM, Maham M Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaf extract and their catalytic activity for the Suzuki–Miyaura coupling in water. J Mol Catal A Chem 396:297–303**(2015)**

[15]. Kumar B, Smita K, Cumbal L, Debut A Ultrasound agitated phytofabrication of palladium nanoparticles using Andean blackberry leaf and its photocatalytic activity. J Sau Chem Soc 19:574–580**(2015)**

[16]. Velmurugan P, Cho M, Lim SS, Seo SK, Myung H, Bang KS, Sivakumar S, Cho KM, Oh BT Phytosynthesis of silver nanoparticles by *Prunus yedoensis* leaf extract and their antimicrobial activity. Mater Lett 138:272–275**(2015)**

[17]. Momeni S, Nabipour I A Simple green synthesis of palladium nanoparticles with *Sargassum* alga and their electrocatalytic activities towards hydrogen peroxide. Appl Biochem Biotechnol 176:1937–1949**(2015)**

[18]. Tao F, Grass ME, Zhang Y, Butcher DR, Renzas JR, Liu Z, Chung JY, Mun BS, Salmeron M, Somorjai GA (2008) Reaction-driven restructuring of Rh-Pd and Pt-Pd core-shell nanoparticles. Science 322:932–934

[19]. Xu JG, Wilson AR, Rathmell AR, Howe J, Chi MF, Wiley BJ Synthesis and catalytic properties of Au-Pd nanoflowers. ACS Nano 5:6119–6127**(2011)**

[20]. Sun D, Zhang G, Huang J, Wang H, Li Q Plant-mediated fabrication and surface enhanced Raman property of flower-like Au@Pd nanoparticles. Materials 7:1360–1369**(2014)**

[21]. Nasrollahzadeh M, Sajadi SM, Rostami-Vartooni A, Khalaj M Green synthesis of Pd/Fe_3O_4 nanoparticles using *Euphorbia condylocarpa* M. *bieb* root extract and their catalytic applications as magnetically recoverable and stable recyclable catalysts for thephosphine-free Sonogashira and Suzuki coupling reactions. J Mol Catalysis A: Chem 396:31–39**(2015)**

[22]. Nasrollahzadeh M, Sajadi SM, Rostami-Vartooni A, Alizadeh M, Bagherzadeh M Green synthesis of the Pd nanoparticles supported on reduced grapheme oxide using barberry fruit extract and its application as a recyclable and heterogeneous catalyst for the reduction of nitroarenes. J Colloid Interface Sci 466:360–368**(2016).**

[23]. Khan M, Albalawi GH, Shaik MR, Khan M, Adil SF, Kuniyil M, Alkhathlan HZ, Al-Warthan A, Siddiqui MRH Miswak mediated green synthesized palladium nanoparticles as effective catalysts for the Suzuki coupling reactions in aqueous media. J Sau Chem Soc. http://dx.doi.org/10.1016/j.jscs.2016.03.008**(2016)**

[24]. Vinodhini. S, Scholastica MaryVithiya. B. Augustine ArulPrasad. T. "Green synthesis of palladium nanoparticles using aqueous plant extracts and its biomedical applications" https://doi.org/10.1016/j.jksus.2022.102017**(2022).**

[25]. Fulya Gülbağça, Ayşenur Aygün, Mehmet Gülcan, Fatih Şen" Green synthesis of palladium nanoparticles: Preparation, characterization, and investigation of antioxidant, antimicrobial, anticancer, and DNA cleavage activities" August 2021Applied Organometallic Chemistry 35(8) DOI: 10.1002/aoc.6272

[26]. Oriana Piermatti *Catalysts* 2021, *11*(11), 1258; https://doi.org/10.3390/catal11111258.

[27]. Petla RK, Vivekanandhan S, Misra M, Mohanty AK, Satyanarayana N Soybean (*Glycine max*) leaf extract based green synthesis of palladium nanoparticles. J Biomater Nanobiotechnol 3:14–19**(2012)**

[28]. Khan M, Khan M, Kuniyil M, Adil SF, Al-Warthan A, Alkhathlan HZ, Tremel W, Tahir MN, Siddiqui MRH Biogenic synthesis of palladium nanoparticles using *Pulicaria glutinosa* extract and their catalytic activity towards the Suzuki coupling reaction. Dalton Trans 43:9026**(2014).**

[29]. Qiong Z, Jin SC, Xiao FL, Hao TB, Jian HJ (2011) Palladium nanaparticles/ chitosan-grafted graphene nanocomposites for construction of a glucose biosensor. Biosens Bioelec 26:3456–3463

[30]. Cacchi S, Caponetti E, Casadei MA, Giulio AD, Fabrizi G, Forte G, Goggiamani A, Moreno S, Paolicelli P, Petrucci F, Prastaro A, Saladino ML Suzuki-Miyaura cross-coupling of arenediazonium salts catalyzed by alginate/ gellan-stabilized palladium nanoparticles under aerobic conditions in water. Green Chem 14:317–320**(2012)**

[31]. Parker HL, Rylott EL, Hunt AJ, Dodson JR, Taylor AF, Bruce NC, Clark JH Supported palladium nanoparticles synthesized by living plants as a catalyst for Suzuki-Miyaura reactions. PLoS One 9:e87192**(2014).**

[32]. Kora AJ, Rastogi L Green synthesis of palladium nanoparticles using gum ghatti (*Anogeissus latifolia*) and its application as an antioxidant and catalyst. Arab J Chem http://dx.doi.org/10.1016/j.arabjc.2015.06.024**(2015)**

[33]. Roopan SM, Bharathi A, Kumar R, Khanna VG, Prabhakarn A Acaricidal, insecticidal, and larvicidal efficacy of aqueous extract of *Annona squamosa* L peel as biomaterial for the reduction of palladium salts into nanoparticles. Colloids Surf B 92:209–212**(2012)**

[34]. Kalaiselvi A, Roopan SM, Madhumitha G, Ramalingam C, Elango G Synthesis and characterization of palladium nanoparticles using Catharanthus roseus leaf extract and its application in the photo-catalytic degradation. Spectrochim Acta Part A 135:116–119**(2015)**

[35]. Anand K, Tiloke. C, Phulukdaree. A, Ranjan. B, Chuturgoon. A, Singh S, Gengan. RM Biosynthesis of palladium nanoparticles by using *Moringa oleifera* flower extract and their catalytic and biological properties. Photochem Photobiol. doi:10.1016/j.jphotobiol.2016.09.039**(2016).**

[36]. Surendra TV, Roopan SM, Arasu MV, Abdullah Al-Dhabi N, Rayalu GM RSM optimized *Moringa oleifera* peel extract for green synthesis of M. oleifera capped palladium nanoparticles with antibacterial and hemolytic property. J Photochem Photobiol B Biol 162:550–557**(2016)**

[37]. Nasrollahzadeh M, Mohammad Sajadi S Pd nanoparticles synthesized *in situ* with the use of *Euphorbia granulate* leaf extract: Catalytic properties of the resulting particles. J Coll Inter Sci 462:243–251**(2016)**

[38]. Manikandan V, Velmurugan P, Park JH, Lovanh N, Seo SK, Jayanthi P, Park YJ, Cho M, Oh BT Synthesis and antimicrobial activity of palladium nanoparticles from *Prunus* x *yedoensis* leaf extract. Mater Lett 185(2016):335–338**(2016)**

[39]. Saravanakumar A, Peng MM, Ganesh M, Jayaprakesh J, Mohankumar M, Jang HT Low-cost and eco-friendly green synthesis of silver nanoparticles using *Prunus japonica* (Rosaceae) leaf extract and their antibacterial, antioxidant properties. Artif Cells Nanomed Biotechnol, http://dx.doi.org/10.1080/21691401.2016.1203795**(2016)**

[40]. Philip D (2011) *Mangifera indica* leaf-assisted biosynthesis of well-dispersed silver nanoparticles. Spectro Acta A: Mol Biomol Spectrosc 78:327–331

[41]. Karuppiah M, Rajmohan R Green synthesis of silver nanoparticles using *Ixora coccinea* leaves extract. Mater Lett 72:367–369**(2014)**

[42]. Stephens IEL, Bondarenko AS, Grønbjerg U, Rossmeisl J, Chorkendorff I Understanding the electrocatalysis of oxygen reduction on platinum and its alloys. Energy Environ Sci 5:6744–6762**(2012).**

[43]. Ye W, Yu J, Zhou Y, Gao D, Wang D, Wang C, Xue D Green synthesis of Pt–Au dendrimer-like nanoparticles supported onpolydopamine- functionalized graphene and their high performancetoward 4- nitrophenol reduction. App Cat B: Environm 181:371–378**(2016)**

[44]. Nasrollahzadeh M, Sajadi SM Green synthesis, characterization and catalytic activity of the Pd/TiO_2 nanoparticles for the ligand-free Suzuki– Miyaura coupling reaction. J Coll Inter Sci 465:121–127**(2016)**

[45]. Sheny DS, Philip D, Mathew J (2013) Synthesis of platinum nanoparticles using dried *Anacardium occidentale* leaf and its catalytic and thermal applications. Spectrochim Acta A Mol Biomol Spectrosc 114:267–271

[46]. Maged S. Al-Fakeh, Samir Osman Mohammed Osman, Malek Gassoumi, Mokded Rabhi, and Mohamed Omer " Characterization, Antimicrobial and Anticancer Properties of Palladium Nanoparticles Biosynthesized Optimally Using Saudi Propolis" Published online 2021 Oct 11. doi: 10.3390/nano11102666**(2021).**

[47]. Soundarrajan C, Sankari A, Dhandapani P, Maruthamuthu S, Ravichandran S, Sozhan G, Palaniswamy N Rapid biological synthesis of platinum nanoparticles using *Ocimum sanctum* for water electrolysis applications. Bioprocess Biosyst Eng 35:827–833**(2012)**

[48]. Moulton MC, Braydich-Stolle LK, Nadagouda MN, Kunzelman S, Hussain SM, Varma RS (2010) Synthesis, characterization and biocompatibility of "green" synthesized silver nanoparticles using tea polyphenols. Nanoscale 2:763–770

[49]. Lu Y, Yuan JY, Polzer F, Drechsler M, Preussner J (2010) In situ growth of catalyticactive AuPt bimetallic nanorods in thermoresponsive core–shell microgels. ACS Nano 4:7078–7086

[50]. Coccia F, Tonucci L, Bosco D, Bressan M, d'Alessandro N (2012) One pot synthesis of lignin-stabilized platinum and palladium nanoparticles and their catalytic behaviours in oxidation and reduction reactions. Green Chem 14: 1073–1078

[51]. Chu C, Su Z Facile synthesis of AuPt alloy nanoparticles in polyelectrolytemultilayers with enhanced catalytic activity for reduction of 4-nitrophenol. Langmuir 30:15345–15350**(2014)**

[52]. Thirumurugan A, Aswitha P, Kiruthika C, Nagarajan S, Nancy CA Green synthesis of platinum nanoparticles using *Azadirachta indica* – An eco-friendly approach. Mater Lett 170:175–178**(2016)**

[53]. Yoshihisa Y, Zhao QL, Hassan MA, Wei ZL, Furuichi M, Miyamoto Y, Kondo T, Shimizu T SOD/catalase mimetic platinum nanoparticles inhibit heat-induced apoptosis in human lymphoma U937 and HH cells. Free Radical Res 45:326–335**(2011)**

[54]. Bendale Y, Bendale V, Paul S, Bhattacharyya SS (2012) Green synthesis, characterization and anticancer potential of platinum nanoparticles bioplatin. Chin J Integr Med 10:681–689

[55]. Sengupta P, Basu S, Soni S, Pandey A, Roy B, Oh MS, Chin KT, Paraskar AS, Sarangi S, Connor Y, Sabbisetti VS, Kopparam J, Kulkarni A, Muto K, Amarasiriwardena C, Jayawardene I, Lupoli N, Dinulescu DM, Bonventre JV, Mashelkar RA, Sengupta S Cholesterol-tethered platinum II-based supramolecular nanoparticle increases antitumor efficacy and reduces nephrotoxicity. Proc Natl Acad Sci U S A 109:11294–11299**(2012)**

[56]. Hou J, Shang J, Jiao C, Jiang P, Xiao H, Luo L, Liu T A core crosslinked polymeric micellar platium(IV) prodrug with enhanced anticancer efficiency. Macromol Biosci 13:954–965**(2013)**

[57]. Mironava T, Simon M, Rafailovich MH, Rigas B (2013) Platinum folate nanoparticles toxicity: cancer vs. normal cells. Toxicol In Vitro 27:882–889

[58]. Wang J, Wang X, Song Y, Zhu C, Wang K, Guo Z (2013) Detecting and delivering platinum anticancer drugs using fluorescent maghemite nanoparticles. Chem Commun (Camb) 49:2786–2788

[59]. Min Y, Li J, Liu F, Yeow EK, Xing B NIR light mediated photoactivation pt based antitumor prodrug and simultaneous cellular apoptosis imaging via upconversion nanoparticles. Angew Chem Int Ed Engl 53:1012–1016**(2014)**

[60]. Pandey A, Kulkarni A, Roy B, Goldman A, Sarangi S, Sengupta P, Phipps C, Kopparam J, Oh M, Basu S, Kohandel M, Sengupta S Sequential application of a cytotoxic nanoparticle and a PI3 K inhibitor enhances antitumor efficacy. Cancer Res 74:675–85**(2014)**

[61]. Alshatwi AA, Athinarayanan J, Subbarayan PV Green synthesis of platinum nanoparticles that induce cell death and G2/M-phase cell cycle arrest in human cervical cancer cells. Mater Sci: Mater Med 26:7**(2015)**

[62]. Smitha SL, Nissamudeen KM, Philip D, Gopchandra KG (2008) Studies on surface plasmon resonance and photoluminescence of silver nanoparticles. Spectrochim Acta A Mol Biomol Spectrosc 71:186–190

[63]. Farabegoli F, Papi A, Bartolini G, Ostan R, Orlandi M (2010)-Epigallocatechin- 3-gallate downregulates Pg-P and BCRP in a tamoxifen resistant MCF-7 cell line. Phytomedicine 17:356–362

[64]. Kalimutho M, Minutolo A, Grelli S, Formosa A, Sancesario G, Valentini A, Federici G, Bernardini S Satraplatin (JM-216) mediates G2/M cell cycle arrest and potentiates apoptosis via multiple death pathways in colorectal cancer cells thus overcoming platinum chemo-resistance. Cancer Chemother Pharmacol 67:1299–12312**(2011)**

[65]. Endo K, Ueno T, Kondo S, Wakisaka N, Murono S, Ito M, Kataoka K, Kato Y, Yoshizaki T Tumor-targeted chemotherapy with the nanopolymer- based drug NC-6004 for oral squamous cell carcinoma. Cancer Sci 104:369–374**(2013)**

[66]. Yang J, Sun X, Mao W, Sui M, Tang J, Shen Y Conjugate of Pt(IV)-histone deacetylase inhibitor as a prodrug for cancer chemotherapy. Mol Pharm 9:2793–2800**(2012).**

Kuda Eswara Rao, et. al. "Green Synthesis of Palladium (Pd) Nanomaterials using Plant Extracts for Catalysis and Biological Applications." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 15(06), (2022): pp 30-36.