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REVIEW

Biogenic synthesis of platinum nanoparticles

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Abstract
There are several existing methods for synthesizing metallic nanoparticles, with the most commonly applied being chemical reduction methods. Recently, the biogenic synthesis of noble metal nanoparticles has been developed. These methods involve biological systems such as bacteria, fungus, and plant extracts. Green and biological methods are economical, eco-friendly, and non-toxic methods of obtaining nanoparticles for possible biomedical applications. Here, we present a short overview of the biogenic synthesis of platinum nanoparticles using plants, plant extracts, bacteria, fungi, and other substances.

Keywords Platinum nanoparticles · Biogenic · Plants · Bacteria · Fungi · Algae

Introduction

There are multiple methods of obtaining platinum nanoparticles, which can be divided into two strategies: top to bottom *(top-down)* and bottom to top (*bottom-up*) (Habibullah et al. 2021; Loza and Epple 2019). The first consists of structurally decomposing a large metal (that is, the bulk material), which has some drawbacks, such as the high energy cost of the equipment, limited control over the size or shape of adjustments, reduced heterogeneity, and increased material homogeneity. Examples of this strategy include photolithography, electron beam lithography, milling techniques, anodizing, and etching with ions and plasma. These processes can produce ligand-free nanoparticles (Figure 1).

Although bottom-up is one of the most common techniques for preparing platinum nanoparticles, which consists of self-assembly of the particles using wet chemical methods, this results in greater reliability in morphology and size. However, one of the most frequently mentioned drawbacks is the presence of impurities from the use of toxic inorganic and organic chemicals that remain in the reaction mixture. As the production of these colloidal metals requires chemical reactions, which involve the reduction of a Pt (II) precursor, such as potassium tetrachloroplatinate (K_2PtCl_4) or platinum (II) bis(acetylacetonate); or a Pt (IV) precursor such as potassium (IV) hexachloroplatinate (K_2PtCl_6) (other examples: chloroplatinic acid $\left(H_2PtCl_6\right)$, platinum (II) chloride $\left(PtCl_2\right)$, tetraammineplatinum(II) nitrate $\left(Pt\left(NH_3\right)_4\left(NO_3\right)_2\right)$, or tetraammineplatinum(II) hydroxide hydrate $\left(Pt\left(NH_3\right)_4(OH)_2 \cdot xH_2O\right.$, tetraammineplatinum (II) chloride hydrate $\left(Pt\left(NH_3\right)_4Cl_2 \cdot xH_2O\right)$, *etc.*) (Chen and Holt-Hindle 2010; Hikosaka et al. 2008; Kankala et al. 2020; Mironava et al. 2013; Shim et al. 2017; Zheng et al. 2013) dissolved in appropriate solvents in the presence of reducing agents (e.g., hydrogen, carbon monoxide, sodium borohydride, ethylene glycol, glycerol, etc.), tensioactive materials or surfactants (polyvinyl alcohol (Asharani et al. 2010), Brij-58 (Shim et al. 2017), cetyl trimethyl ammonium bromide (Lee et al. 2006), sodium dodecyl sulfate (Mohammadi et al. 2013), etc.), ligands (e.g., peptides, proteins, nucleic acids, small molecules, etc.), or stabilizing/coating polymers (e.g. polyvinylpyrrolidone (Herricks et al. 2004; Koebel et al. 2008), hyaluronic acid (Zhu et al. 2017), alginic acid, thiols, etc.) that help reduce dispersion and prevent aggregation and may or may not endanger complex biological systems. Thus, we must carefully consider the design depending on the objectives we want to achieve since the biological and chemical applications are diverse (Fig. 2) (Liu et al. 2014; Stepanov et al. 2014; Yamada et al. 2015).

Among these strategies, we find a set of methods such as chemical or electrochemical precipitation, sol–gel, laser-induced pyrolysis, chemical vapor deposition (CVD), synthesis by plasma, or flame spraying (Habibullah et al. 2021). These ideas, however, have not remained stagnant; rather,

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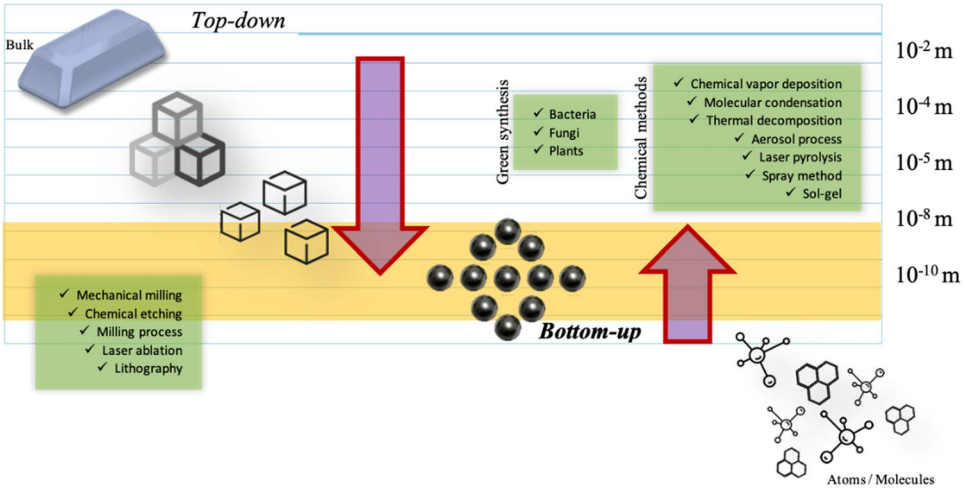

Fig. 1. Convergence of top-down and bottom-up physical and chemical methods for nanoparticle formation

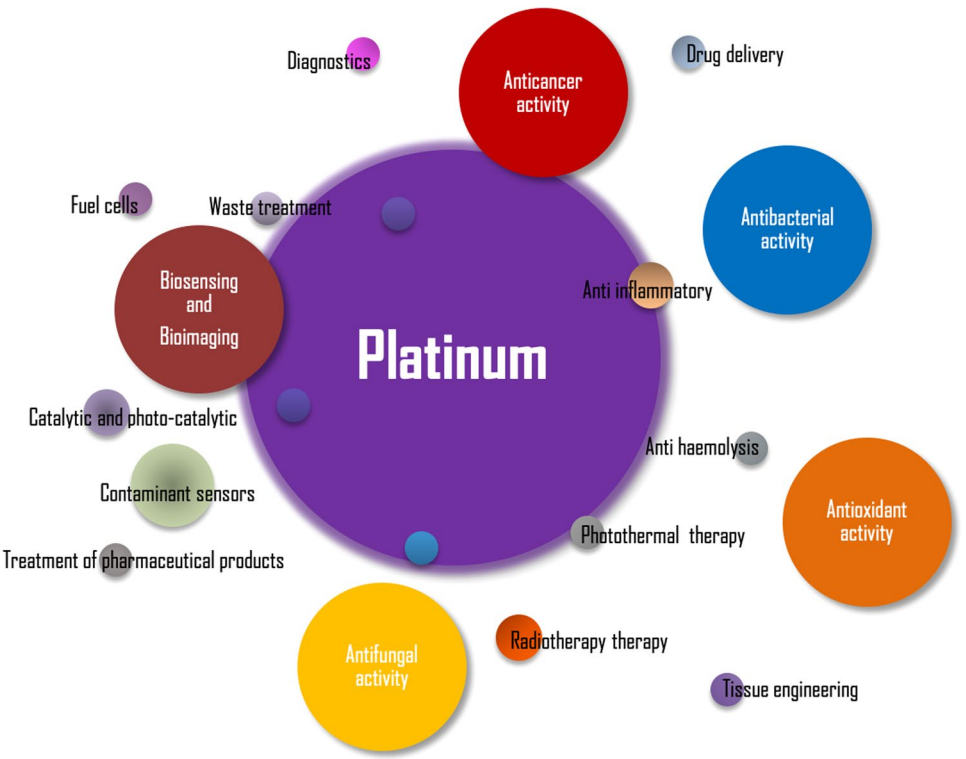

Fig. 2. Multiple applications for platinum nanoparticles

they have formed new links with biological studies with the aim of obtaining environmentally friendly syntheses since living beings interact with the environment (Mohanpuria et al. 2008; Pedone et al. 2017; Siddiqi and Husen 2016). Modification and optimization have been used to obtain high-quality products, directing responses through product safety with the help of bio-assisted synthesis and the use of green chemistry. The sizes and shapes of the nanoparticles are diverse, since all syntheses use variables such as pH, temperature, reducing agents (chemical or biological), and the concentration of the platinum precursor compound, making endless products with different characteristics (Jameel et al. 2020).

Due to their unique physicochemical properties, e.g., catalytic, magnetic, and optical properties, Pt nanoparticles have potential technological interest (Chen and Holt-Hindle 2010; Elder et al. 2007). The latter are of utmost importance for biomedical use since, from the catalytic perspective, platinum is inert and does not corrode within the human body, endowing it with the ability to inhibit cell division in mammals and in some bacteria (Jan et al. 2021; Puja and Kumar 2019). Regarding optical properties, platinum nanoparticles

are distinguished by the presence of a very distinctive localized surface plasmon resonance in the UV–Vis region, a characteristic that is not evident in the bulk material. On the other hand, we find the efficiency of heat generation is higher than in other nanoparticles (del Valle et al. 2020; Sadrolhosseini et al. 2019; San et al. 2013). Therefore, Pt nanoparticles could be an alternative treatment in hyperthermia therapy (Fang et al. 2020; Zhao et al. 2019). These properties have made platinum nanomaterials significant candidates for biomedical applications in catalysts, sensors, nanomedicine, anti-inflammatories, enzymes, and pharmaceutical immobilization, among others (Madlum et al. 2021; Naseer et al. 2020). Recently, the effect of Pt nanoparticles on human cells for cancer therapy was investigated (Almeer et al. 2018; Gurunathan et al. 2019, 2020; Ismail and Al-Radadi 2017; Kankala et al. 2020;). The increased number of biological and biomedical applications has necessitated the development of new synthesis methods.

Biological synthesis methods

Methods for the green synthesis of nanoparticles are ecological routes that represent an alternative to chemical and physical methods. These methods eradicate or reduce the generation of dangerous substances. Various metal nanoparticles have been synthesized using plant phytochemicals as reducing agents and stabilizers without the use of costly and toxic chemicals. This green synthesis involves biological methods using plants, enzymes, biomolecules, agricultural and industrial waste products, microorganisms, or algae (Alshatwi et al. 2015; Ojo et al. 2021). Nanobiotechnology is the application and use of nanotechnology in life sciences, including in molecular diagnostics, drug discovery, drug delivery, and the development of nanomedicine (Jain 2005; Rahman et al. 2019). Green nanobiotechnology should be defined as synthesizing nanoparticles or nanomaterials using biological routes with the help of various biotechnological tools (Patra and Baek 2014).

Biological or bio-assisted synthesis methods are very diverse as they require biological organisms (unicellular or multicellular), which act as "bio-laboratories" or "nano-factories" for producing biogenic nanoparticles (Jan et al. 2021; Jeyaraj et al. 2019; Pedone et al. 2017; Puja and Kumar 2019). Metallic nanoparticles are synthesized through metabolic pathways or using derivatives (e.g., extracts, wastes, animal products) of these organisms. Syntheses can occur intracellularly or extracellularly (Ali et al. 2015; Puja and Kumar 2019; Sharma et al. 2019). Using these methods, safer, more ecological, and more environmentally friendly protocols have been designed. However, these methods also have disadvantages (Jameel et al. 2020; Narayanan and Sakthivel 2010; Sharma et al. 2019). Particular disadvantages include the fact that this method is not easy to control in terms of designing the shape, size, crystal growth, and stability, and the possibility of finding endotoxins when the reaction has been completed (Jameel et al. 2020). However, the advantages are that biological organisms can be cultured easily and can manifest high intracellular absorption of metallic salts, and the fact that it is easier to manage the biomass and waste that these may generate than the toxic reagents derived from the chemical pathways described previously (Fahmy et al. 2020; Naseer et al. 2020; Rai and Duran 2011).

Biological synthesis methods are frequently used to prepare a wide variety of nanoparticles, the most common among them being Au and Ag (Cardoso-Avila et al. 2021; Kalimuthu et al. 2020; Tarannum et al. 2019; Tepale et al. 2019; Zamiri et al. 2011). Other metallic and oxide nanoparticles are also reported with these methods, like Pd, Cu, Fe, CuO, Fe_3O_4, ZnO TiO_2, NiO, CeO_2, etc. (Ishak et al. 2019; Marouzi et al. 2021; Singh et al. 2018; Sabouri et al. 2019, 2020a, b).

Here, we briefly review the use of microorganisms such as bacteria, fungi, and algae and complex systems including plants, along with products derived from all of these, for the synthesis of platinum nanoparticles (Fig. 3, Table 1).

Plant-mediated synthesis

These biogenic pathways can be targeted in two ways. The first is by intracellular synthesis, where metallic nanoparticles can bioaccumulate. The second is extracellular synthesis, where platinum accumulation is mediated by plant biomass (e.g., agro-industrial waste) so that all the components of the plant from the roots, stem, bark, leaves, flowers, fruits, and even peels and bio-derivatives (e.g., extracts, gums, etc.) obtained from these components are employed. All parts of the plant have biomolecules to a greater or lesser extent, for example, proteins, enzymes, flavonoids, polyphenols, cannabinoids, terpenoids, glycosides, sugars, alcohols, aldehydes, amines, carbonyls, etc., that aid in the reduction of platinum salts and their stabilization for the formation of metal nanoparticles. An advantage of this method is that it eliminates elaborate stages in the maintenance process that occur in cell cultures. Thus, the use of plants can be suitably scaled up for large-scale synthesis.

Many living plants have been shown to function as aids in the formation of nanoparticles by absorbing metal ions; the first report of this occurrence was in 2002 by Gardea-Torresdey et al. when it was demonstrated that gold nanoparticles had formed in the roots and shoots of alfalfa plants that grew in an environment rich in potassium tetrachloroaurate ($KAuCl_4$), thus intracellularly initiating the bioreduction of the metal salt to form insoluble

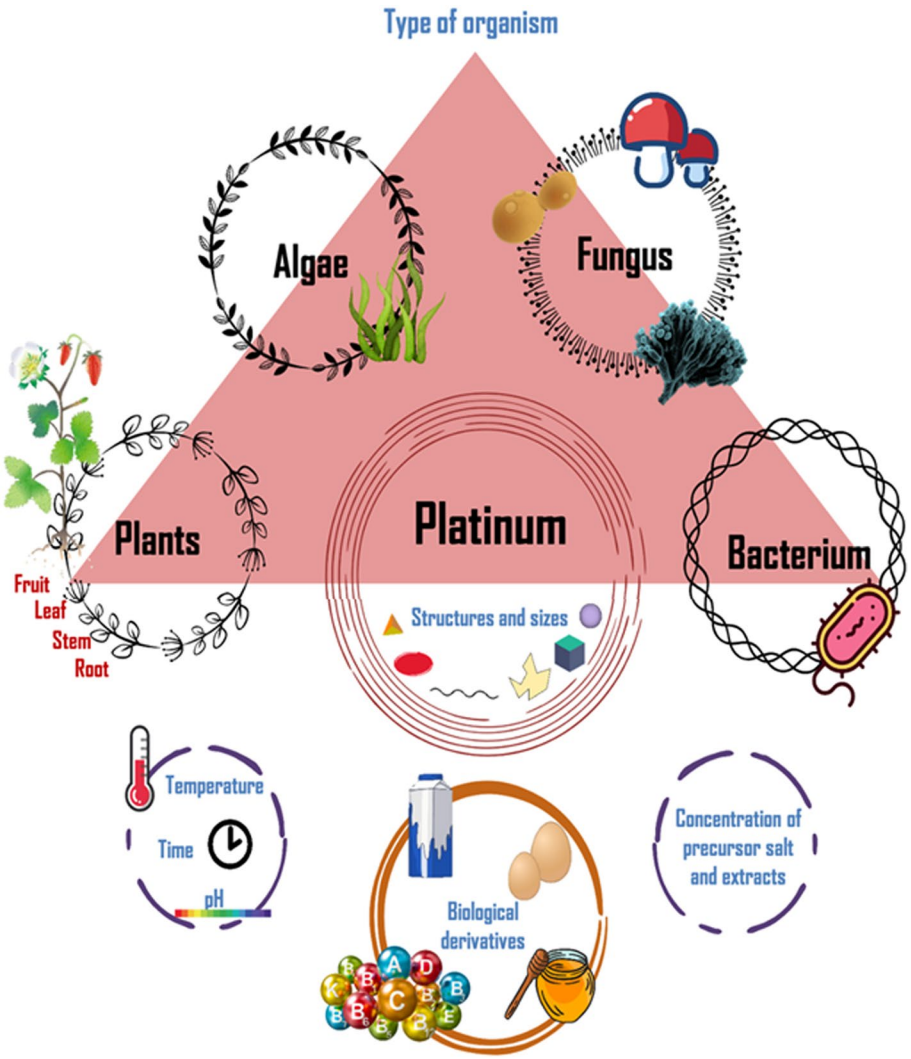

Fig. 3. Factors that affect the biosynthesis of platinum nanoparticles and the organisms and by-products that are used to obtain them

compounds (e.g., nanoparticles) (Gardea-Torresdey et al. 2002). It was later shown that alfalfa could also form silver nanoparticles when exposed to a solid medium rich in silver salts (Gardea-Torresdey et al. 2002, 2003). Therefore, Bali et al. (2010) selected two facultative metallophyte plants (*Medicago sativa* and *Brassica juncea*), as it had previously been shown that both species accumulated precious metals; thus, the distribution of Pt in vivo in the different tissues of these organisms was determined for the first time using proton-induced X-ray emissions. In both plants, Pt concentration increased by raising aqueous substrate concentration, prolonging exposure time, and lowering pH to 2 and 3 for *Medicago sativa* and *Brassica juncea*, respectively. Pt nanoparticles between 3 and 100 nm with varied morphology were formed due to the action of local metabolites (Bali et al. 2010). Despite this, information on the intracellular biosynthesis of Pt nanoparticles in living plants is still scant, but it has been possible to accumulate information about synthesis by using various products and by-products of plants, as presented in Table 1 (Naseer et al. 2020).

The first study to focus on the green chemistry of Pt nanoparticles was that of Song et al. who discussed the biosynthesis of this metal with plant extracts in 2010 (Song et al. 2010) using an extract from a *Diospyros kaki* leaf that functioned as a medium and a reducing agent in the ecological extracellular synthesis of biogenic Pt nanoparticles in an aqueous solution of $K_2PtCl_6 \cdot 6H_2O$ with a conversion from platinum ions to platinum nanoparticles of over 90% and a concentration of foliar biomass > 10% at 95 °C. The microscopic studies reported for transmission electron microscopy (TEM) showed oscillations between 2 and 20 nm, giving a mixture of shapes that included spheres and disks, whereas the Fourier transformed infrared spectroscopic studies revealed the presence of metabolites such as terpenoids, where the reduction process is not an enzyme-mediated process because the nanoparticle formation temperature exceeds 95 °C. Therefore, these techniques show

Table 1. Biogenic synthesis of platinum nanoparticles

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application/cell line	Year
Plants								
Diospyros kaki	Leaf	Extracellular	Spheres and plates	02–12	Terpenoids	–	–	Song et al. (2010)
Cochlospermum gossypium	Gum	Aqueous	Spheres	2.4	Amino acids	–	–	Vinod et al. (2011)
Ocimum tenuiflorum *Euphorbia neriifolia* *Sesbania grandiflora* *Piper betle* *Asteracantha longifolia*	Leaf	Extracellular	Irregular	137.5	–	–	Calf thymus DNA and honey Anticancer activity /A375 and peripheral blood mononuclear cells (PBMC)	Bendale et al. (2012)
Ocimum sanctum	Leaf	Extracellular	Irregular	23	Terpenoids, sugars and proteins	–	Water electrolysis	Soundarrajan et al. (2012)
Camellia sinensis	Leaf	Extracellular	Spheres	02 –10	Polyphenols and terpenoids	–	–	Sanchez-Mendieta and Vilchis-Nestor (2012)
Bacopa monnieri	Leaf	Extracellular	Spheres	05–20	Flavonoids and proteins	–	Neuro-rescuer	Nellore et al. (2013)
Cacumen platycladi	All biomass	Extracellular	Spheres	2.4±0.8	Sugars and flavonoids	–	–	Zheng et al. (2013)
Anacardium occidentale	Leaf	Extracellular	Irregular rods	–	Secondary metabolites and proteins	–	Catalytic activity and thermal conductivity	Sheny et al. (2013)
Terminalia chebula	Fruit	Extracellular	Quasi-spherical	<04	Polyphenols	–	–	Mohan et al. (2013)
Asparagus racemosus	Root	Extracellular	Irregular	01–06	–	–	–	Raut et al. (2013)
Piper betle	Leaf	Extracellular	Spheres	2.1±0.4	Protein	–	Aquatic organisms */Daphnia magna/*	Rajasekharreddy and Rani (2014)
Punica granatum	Peel	Extracellular	Spheres	16–23	Polyphenols		Catalytic activity	Dauthal and Mukhopadhyay (2014)
Dioscorea bulbifera	Tuber	Extracellular	Spheres	02–05	Polyphenols	–	Anticancer activity /HeLa/	Ghosh et al. (2015)
Orange	Peel	Extracellular	Amorphous	23	Thiamine	–	Catalytic activity	Castro et al. (2015)
Fumaria officinalis	All the herb	Extracellular	Hexagonal and Pentagonal	20–30	Alkaloids, flavonoids and phenolic acids	–	Catalytic activity	Dobrucka (2016a)
Bidens tripartita	All the herb	Extracellular	Aggregates and rods	10	Phenols	–	–	Dobrucka (2016b)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application/cell line	Year
Quercus glauca	Leaf	Extracellular	Spheres	05–15	Flavonoids, tannins and glycosides	–	Electrochemical properties	Karthik et al. (2016)
Lantana camara	Leaf	Extracellular	Monodisperse spheres	35	–	Ascorbic acid	–	Mavukkandy et al. (2016)
Azadirachta indica	Leaf	Extracellular	Polydisperse spheres	05–50	Terpenes and sugars	–	–	Thirumurugan et al. (2016)
Prunus x yedoensis	Gum	Extracellular	Spherical and oval	10–50	Flavonoids and polysaccharides	–	Antifungal activity */Colletotrichum acutatum/ /Cladosporium fulvum/ /Didymella bryoniae/ /Phytophthora drechsleri / /Phytophthora capsici /*	Velmurugan et al. (2016)
Maytenus royleanus	Leaf	Extracellular	Spheres	05	Flavonoids and phenolic compounds	–	Anticancer activity /A549/ Catalytic activity	Ullah et al. (2017)
Phoenix dactylifera	Fruit (ajwa)	Extracellular	Spheres	1.3–2.6	Flavonoids and phenolic compounds		Anticancer activity /HCT-116/ /MCF-7/ /HePG-2/ Antibacterial activity *Escherichia coli Bacillus subtilis*	Ismail and Al-Radadi (2017)
Barleria prionitis	Leaf	Extracellular	Spheres	01–02	Polyphenols, alcohols and proteins	–	Anticancer activity /MCF–7/	Rokade et al. (2017)
Eichhornia crassipes	Leaf	Extracellular	Spheres	03.74	Polysaccharides, alkaloids	–	–	Leo and Oluwafemi (2017)
Ocimum tenuiflorum	Leaf	Extracellular	Aggregate and irregular	02	Polysaccharides and proteins	–	–	Prabhu and Gajendran (2017)
Taraxacum laevigatum	All the plant	Extracellular	Spheres	02–07	Phenolic compounds, proteins, flavonoids and saponins	–	Antibacterial activity */Bacillus subtilis/ /Pseudomonas aeruginosa/*	Tahir et al. (2017)
Sapindus mukorossi	Pericarp	Extracellular	Spheres	02–19	Saponins and flavonoids	–	–	Kumar et al. (2017)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application/cell line	Year
Withania somnifera	Leaf	Extracellular	Aggregate and spheres	12	Terpenes	–	Anti-diabetic Studies /Sprague–Dawley rats/	Li et al. (2017)
Punica granatum	Peel	Extracellular	Spheres	20.12	–	–	Anticancer activity /MCF-7/	Sahin et al. (2018)
Punica granatum	Aril	Extracellular	Semi-crystalline	11	Alcohols and phenolic compounds	–	Anticancer activity /MCF-7/ / MDA-MB-231/	Jha et al. (2018)
Azadirachta indica	Leaf	Extracellular	Spheres	24.6	–	–	Cytotoxicity /HEK293/	Almeer et al. (2018)
Gloriosa superba	Tuber	Extracellular	Spheres	10	Alcohols and phenolic compounds	–	Anticancer activity /MCF-7/	Rokade et al. (2018)
Antigonon leptopus	Leaf Stalk Root	Extracellular	Monodisperse and polydisperse spheres	05–190	Polysaccharides and proteins	–	–	Ganaie et al. (2018)
Mimosa pudica	Leaf	Extracellular	Spheres	< 02	Tannins and proteins	–	Conversion chemistry Catalytic decomposition	Henam et al. (2018)
Jatropha gossypifolia and *Jatropa glandulifera*	Leaf	Extracellular	Rectangular, cubic and hexagonal and irregular spherical plates	100–200	$-SO_2$		Antibacterial activity /Escherichia coli/ /Klebsiella pneumonia/ / Pseudomonas aeruginosa/ /Bacillus licheniformis/ / Staphylococcus epidermidis/ / Staphylococcus aureus/	Jeyapaul et al. (2018)
Ginger and turmeric	Powders	Extracellular	Amorphous	–	Phenolic compounds.	–	Catalytic activity	Sahin and Gubbuk (2019)
Orange	Peel	Extracellular	Spheres	1.4–4.0	–	–	Electrochemical analysis	Karim et al. (2019)
Ononidis radix	Root	Extracellular	Spheres and hexagons	04	Flavonoids, isoflavonoids and esters	–	Anticancer activity /A549/	Dobrucka et al. (2019)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application/cell line	Year
Phoenix dactylifera	Fruit	Extracellular	Spheres	1.3–2.6	Flavonoids and polyphenols	–	Anticancer activity /HCT-116/ /MCF-7/ /HePG-2/ Antibacterial activity *Escherichia coli* *Bacillus subtilis*	Al-Radadi (2019)
Xanthium strumarium	Leaf	Extracellular	Cubic to rectangular	22	–	–	Anticancer activity /HeLa/ Antibacterial activity */Escherichia coli/* */Klebsiella pneumoniae/* */Pseudomonas aeruginosa/* */Staphylococcus aureus/* */Bacillus subtilis/* Antifungal activity */Candida albicans/* */Candida tropicalis/* */Candida parapsilosis/* */Aspergillus flaves/* */Aspergillus niger/*	Kumar et al. (2019)
Heterotheca inuloides	All the plant	Supported on bovine bone powder	Quasi-spherical	03–40	–	–	Catalytic activity	Gama-Lara et al. (2019)
Phoenix dactylifera	Fruit	Extracellular	Quasi-spherical	2.3–03	Flavonoids, amino acids, phenols, vitamins and minerals		Hepatotoxicity activity */Wister rats/*	Al-Radadi and Adam (2020)
Tragia involucrata	Leaf	Extracellular	Spheres	10	Polyphenols, alkaloids, flavonoids and proteins	–	Anticancer activity /HeLa/ Antibacterial activity */Escherichia coli/* */Staphylococcus aureus/*	Selvi et al. (2020)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application/cell line	Year
Nigella sativa	Seed extract	Extracellular	Spheres	01–06	–		Anticancer activity /MDA-MB-231/ /HeLa/ Antibacterial activity */Escherichia coli/* */Enterobacter aerogenes /* */Pseudomonas aeruginosa/* */Salmonella kentucky/* */Staphylococcus aureus/* */Staphylococcus epidermidis/* */Streptococcus alpha hemolyticus/* */Enterococcus faecium/* */Listeria monocytogenes/*	Aygun et al. (2020)
Nymphaea alba	Flowers	Extracellular	Semispherical and aggregates	35	Saponins, flavonoids, glycoside, alkaloid, tannin and terpenoids	–	Electrocatalytic reduction	
Saccharum officinarum	Bagasse extract	Extracellular	Spheres and mild agglomerated	05±02	Phenolic compounds and flavonoids	–	Antioxidant activity Electrocatalytic oxidation	Ishak et al. (2021)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Type of use		Application // cell line	Year
					Reducers	Stabilizing		
Derivatives of natural substances "green reagents"								
Poly (acrylic) acid (PAA)	Solution	–	Spheres	3	Yes	Yes	Hadrontherapy /Vector pBR322/	Porcel et al. 2010)
Trisodium citrate	Solution	–	Spheres	34	Yes	SDS	Anticancer activity /MCF-7/ /HepG-2/	Mohammadi et al. 2013)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Type of use		Application // cell line	Year
					Reducers	Stabilizing		
Synthetic component of *Camellia sinensis*	Sheets	Extracellular	Flower	30–60	Tea Polyphenol (TPP)	Tea Polyphenol (TPP)	Anticancer activity /SiHa/	Alshatwi et al. 2015)
Gallic acid	Solution	–	Spheres	01–30	Yes	Yes	–	Ko et al. 2015)
Chlorogenic acid	Solution	–	Spheres	16.9±04.7 13.3±04.0 10.8±03.4 07.5±02.3	Yes	Yes	Antioxidant activity	Chen et al. 2021)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application // cell line	Year
Fungi								
Alternaria alternata	Culture filtrate	Extracellular	Quasi-spherical, rectangular, tetrahedral, and hexagonal	50–315	Proteins	–	–	Sarkar and Acharya 2017)
Penicillium chrysogenum (KACC 425892)	Culture filtrate	Extracellular	Spheres	8.5–15	Carbohydrates or proteins	–	Anticancer activity */myoblast C2C12/* Antibacterial activity */Escherichia coli/ /Staphylococcus aureus/ /Staphylococcus pyogenes/ /Enterococcus faecalis/*	Subramaniyan et al. 2018)
Bacteria								
Plectonema boryanum	Aqueous solution	Intracellular and extracellular	Amorphous spheres	30–300	Polysaccharides Proteins	–	–	Lengke et al. 2006)
Shewanella algae	Aqueous solution	Periplasm	Spheres	5	Lactate Enzyme	–	–	Konishi et al. 2007)
Acinetobacter calcoaceticus	Aqueous solution	Intracellularly	Monodisperse	02–03	Proteins	–	–	Gaidhani et al. 2014)
Halomonadaceae, Bacillaceae y *Idiomarinaceae*	–	Intracellular and extracellular	–	09–30 Pt(II) 11 –13 Pt (IV)	H_2	–	–	Maes et al. 2016)
Streptomyces sp.	Aqueous extract	Extracellular	Spheres	20–50	Protein	–	Anticancer activity /MCF-7/	Baskaran et al. 2017)
Protists and others								

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application // cell line	Year
Padina gymnospora	Aqueous extract	Extracellular	Spheres, tetrahedral and truncated octahedral	05–50	Carbohydrates and proteins	PVP	Antibacterial activity */Escherichia coli* (MTCC 1687)/ */Klebsiella pneumoniae* (MTCC 7407)/ */Lactococcus lactis* (MTCC 440)/ */Salmonella typhi* (MTCC 733)/ */Staphylococcus aureus* (MTCC 96)/ */Streptococcus mutans* (MTCC 890)/ */Streptococcus pneumoniae* (MTCC 1936)/ Hemolytic activity	Ramkumar et al. 2017)
Botryococcus braunii	Aqueous extract	Extracellular	Amorphous	86.96	Proteins, polysaccharides, amides and fatty acids.	–	Antibacterial activity */Pseudomonas aeruginosa (MTCC 441)/ /Escherichia coli (MTCC 442)/ /Klebsiella pneumoniae (MTCC109)/ /Staphylococcus aureus (MTCC 96)/* Antifungal activity */Fusarium oxysporum (MTCC 2087)/* Antioxidant activity	Arya et al. 2020)

Table 1. (continued)

Scientific name	Plant section or derivative	Bioaccumulation	Structure	Size (nm)	Bioactives present	Reducers or post-synthesis stabilizers	Application // cell line	Year
Halymenia dilatata	Aqueous extract	Extracellular	Spheres	13.1	Phytochemical constituents	–	Anticancer activity /MDA-MB-231/ Antibacterial activity */Streptococccus pneumoniae/ /Aeromonas hydrophila/*	(Sathiyaraj et al. 2021)
Biogenic substances								
Vitamin B_2	Solution	Suspension	Nanospheres Nanorods Nanowires	< 10	Vitamin (B_2)	Set of solvents	–	Nadagouda and Varma 2006)
Nanocrystalline cotton cellulose	Solution	Suspension	Nanofibers	21	Cellulose	CO_2	–	Benaissi et al. 2010)
Wood	Suspension	Suspension	Spheres Spherical nanoclusters Cubes	02.3 ± 0.5 21.5 ± 5.2 15.2 ± 2.9	Lignin Hemicellulose Cellulose	–	Catalytic activity	Lin et al. 2011)
Honey bee	Solution	Suspension	Quasi-spherical Nanowires	2.2 05–15	Protein	–	Catalytic activity	Venu et al. 2011)
Lignin and fulvic acid	Solution	Suspension	Spheres	06–08	Muconic acid Esters Vanillin Other organic derivatives	–	Catalytic activity	Coccia et al. 2012)
Bacterial cellulose matrix	Matrix	Suspension	Membrane with spheres	6.3–9.3	Cellulose	H_2	–	Aritonang et al. 2014)
Hemicellulose and lignin	Suspension	Suspension	Irregular	< 10	Phenols	–	–	Lin et al. 2016)
Sheep's milk	Milk	Suspension	Spheres	9.0	Protein	–	–	Gholami-Shabani et al. 2016)
Quail egg yolk	Yolk	Suspension	Spheres	7.0–50	Vitamins and proteins	–	–	Nadaroglu et al. 2017)
Chitosan	Exoskeleton	Suspension	Spheres	1.4–1.6	Amino polysaccharides	–	Catalytic activity	Nguyen et al. 2019)

how the modification of incubation temperature, concentration of foliar extract, and metallic ions influence the resulting nanoparticles' yield, size, and shape.

Plant extracts from *Taraxacum laevigatum*, which is a medicinal plant, had a high content of phenolic biomolecules that were the principle reducing and stabilizing agents of Pt nanoparticles (Tahir et al. 2017). The obtained Pt nanoparticles had high antibacterial activity against two bacterial species, *B. subtilis* and *P. aeruginosa*.

A leaf extract from *Ocimum sanctum* (tulsi) has also been used as a reducing agent in the synthesis of Pt nanoparticles; tulsi leaves had abundant tannins, such as gallic acid and chlorogenic acid, and alkaloids, glycosides, and saponins (Soundarrajan et al. 2012).

Another plant with abundant phytoconstituents is the *Carica papaya*, which contains phenolic compounds, tocopherol, ascorbic acid, flavonoids, and reducing sugars. A leaf extract of this plant has been used in the green synthesis of Pt nanoparticles and bimetallic aurium@platinum nanoparticles. The metabolites in *C. papaya* leaf extract played a crucial role in the bioreduction of precursor metals, especially polyphenolic compounds that were also responsible for stabilizing and capping the nanoparticles (Olajire and Adesina, 2017). The proposed reaction mechanism is presented in Fig. 4.

In addition to the extracts, the powder of dried leaves has also been used in the synthesis of platinum nanoparticles, as reported by Sheny et al. (2013). Dried leaf powder of *Anacardium occidentale* was used, and the effect of different amounts of leaf powder (50, 100, 200, 300, and 400 mg) on the formation of nanoparticles was investigated. The amount of leaf powder determined the size of the particles; a smaller amount of powder seems to be adequate for the formation of small rod-shaped Pt nanoparticles (Sheny et al. 2013).

The variation in pH and temperature also has consequences on the size and shape of the nanoparticles. The synthesis of Pt nanoparticles using herbal *Bidens tripartita* extract has been reported. The reaction was maintained at 90 °C for 8 hours with a pH of 8 to ensure the reduction of Pt^{4+} to Pt^{0}. This pH facilitated the formation of more stable Pt nanoparticles; the particles showed an irregular rod shape with a size of 4 nm (Dobrucka, 2016b).

Algae-mediated synthesis of platinum nanoparticles

The use of algae for the green synthesis of nanoparticles has the advantages that it is a low-cost raw material, has a large number of secondary metabolites, and is free of secondary

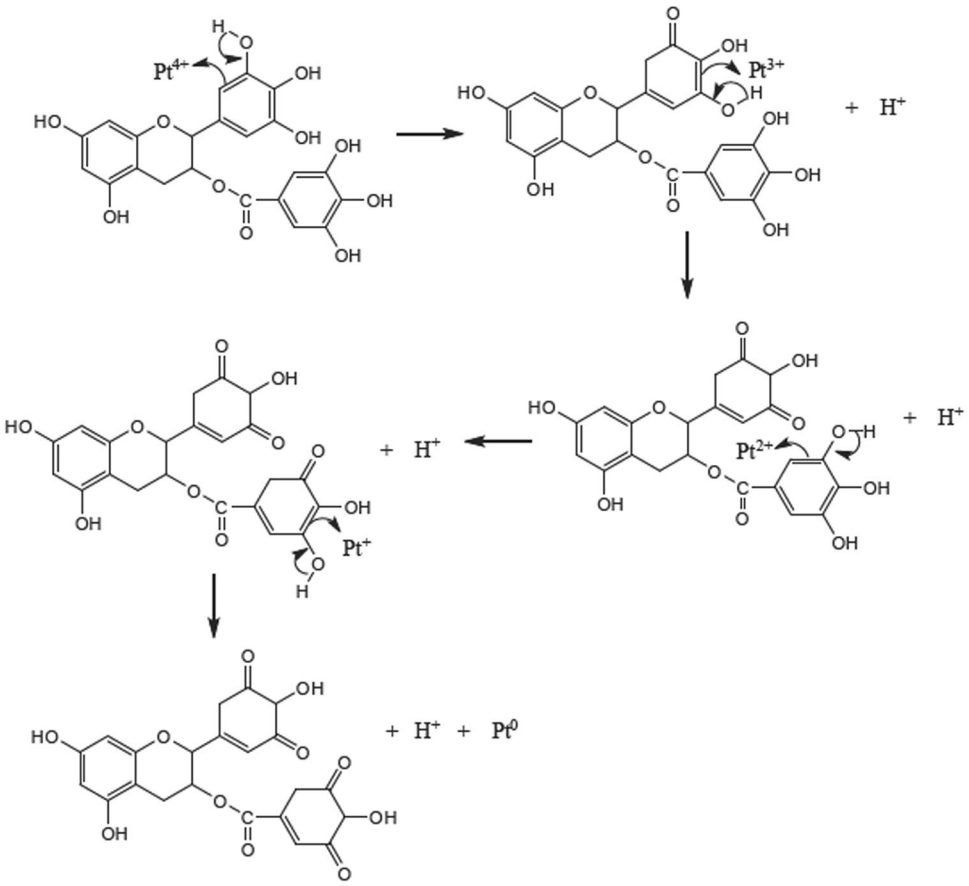

Fig. 4. Proposed mechanism for the bioreduction of Pt^{4+} to Pt atom by a typical polyphenolic compound in *C. papaya* (Olajire and Adesina 2017. Reproduced under Creative Commons Attribution CC-BY 4.0)

contamination. The green synthesis of platinum nanoparticles has been reported using the brown algae *Padina gymnospora*, which is abundant on the coasts of the Ramanathapuram district of the state of Tamil Nadu, India (Shiny et al. 2014). The obtained Pt nanoparticles had a spherical shape in the size range of 5 to 20 nm. Ramkumar et al. (2017) also used this alga for the production of platinum nanoparticles with a truncated octahedral shape and a size range of 5 to 50 nm.

Stable palladium and platinum nanoparticles were produced using extracts of the green alga *Botryococcus braunii* (Arya et al. 2020). The green-synthesized nanoparticles exhibited antimicrobial activity against Gram-positive and Gram-negative bacterial strains, antifungal activity against a fungus, and antioxidant activity.

Synthesis of Pt nanoparticles mediated by fungi

Among living organisms, fungi are now estimated to account for approximately 0.8 to 1.5 million species on the planet, of which 100,000 have been described (Rai et al. 2009; Tedersoo et al. 2014). We have taken particular advantage of their secondary metabolites, which are associated with different structures (e.g., terpenoids, alkaloids, quinones, xanthones, peptides, steroids, flavonoids, phenols, and phenolic compounds), meaning that interest has turned to considering them as an alternative method for the production of nanoparticles, on both small and large scales in laboratories and industries, respectively (Argumedo-Delira et al. 2020; Srivastava 2019). Fungi have the ability to bioaccumulate and tolerate metals thanks to their large secretions of proteins and enzymes. Thus, we were able to use them to synthesize metallic nanoparticles, avoiding agglomerations of particles by using either extracellular or intracellular processes (dependent on metabolism) and the fact that these species require only simple means for supervenience and proliferation, making subsequent biomass processing easy—which is of great economic advantage (Argumedo-Delira et al. 2020; Subashini and Bhuvaneswari 2018).

In 2006, T. Riddin et al. began work on the first protocol for obtaining platinum nanoparticles using *Fusarium oxysporum* fungi (Riddin et al. 2006). The fungal strain was evaluated and found to be successful for the inter and extracellular production of Pt nanoparticles in a size range of 10–100 nm with varying shapes (circular, triangular, hexagonal, square, and rectangular) according to TEM studies. The effects of temperature and concentration of hexachloroplatinic acid $\left(H_2PtCl_6\right)$ and pH during the synthesis of the material were studied. Compared to intracellular synthesis, extracellular synthesis is more advantageous due to the simple post-processing techniques involved. Furthermore, intracellular synthesis requires advanced instruments to extract nanoparticles from biomass (Riddin et al. 2006). Syed and Ahmad (2012) reported the extracellular synthesis of stable Pt nanoparticles using the same microorganism. They showed that when working at room temperature, morphology remains spherical and size ranges between 15 and 30 nm, as shown by TEM analysis. It is therefore apparent that temperature plays an important role in the shape, as already mentioned (Syed and Ahmad 2012). Thus, production of nanoparticles depends mostly on the type of fungus involved and consequently on abiotic factors (temperature, pH, metal ions, and time) (Jameel et al. 2020).

Castro-Longoria et al. (2012) reported the use of the *Neurospora crassa* fungus for the intracellular synthesis of nanoparticles (4–35 nm) at room temperature. The material described formed quasi-spherical and monocrystalline nanoaggregates with a mean size between 20 and 110 nm. Similar results were obtained using fungal extracts to produce Pt nanoaggregates at a range of 17–76 nm, so it can be used as a reducing and stabilizing agent for the synthesis of Pt nanoparticles (Castro-Longoria et al. 2012).

In 2018, Subramaniyan et al. synthesized Pt nanoparticles using the free cell culture of *Penicillium chrysogenum* as a reducer, which was treated in two different environments (normal gravity and micro-gravity), obtaining spheres with a diameter of 15 nm and 8.5 nm, respectively, and evaluating its toxic effect on the mouse myoblast cell line (C2C12). Results showed that cytotoxicity depends on the concentration of the Pt nanoparticles; a decrease in cell viability (apoptosis) is caused by surface stress and the release of ions, which causes an increase in the generation of reactive oxygen species (Subramaniyan et al. 2018). In this way, in 2019 Gupta and Chundawat analyzed the antimicrobial potential and antioxidant activity of Pt nanoparticles synthesized from extracts of *Fusarium oxysporum,* where the hydrogenase enzyme, which behaves as an electron shuttle with excellent redox properties, is already known to be present. This fungus is thus able to achieve this nanoeffect on metal ions (Gupta and Chundawat 2019), where they show good to moderate antibacterial activity against various pathogens, affirming that biosynthesized Pt nanoparticles are non-toxic (Nida and Khan 2017; Durán et al. 2005). Argumedo-Delira et al. (2020) used a set of filamentous fungi with the aim of evaluating the effect of groups of precious metals on them. Platinum specifically was shown not to have secondary effects on their growth, and so Pt nanoparticles can be considered synthetic alternatives for possible biotechnological or biomedical applications. Notably, however, many organisms of this type can still be considered pathogens as they release mycotoxins, phytotoxins, etc., that can cause side effects in animals and humans (Argumedo-Delira et al. 2020).

Bacterium-mediated synthesis

It is well known that many organisms, both unicellular and multicellular, produce inorganic materials intracellularly or extracellularly (Bhattacharya and Gupta 2005; Singh and Singh 2019). Therefore, over the past two decades, research has focused on bacteria as a potential alternative for nanomaterial biosynthesis, employing their natural defense mechanisms that have evolved over time under extreme environmental conditions (Riddin et al. 2010; Solak et al. 2017). These stress conditions have allowed these microorganisms to develop survival mechanisms to overcome particular problems, including the toxicity caused by high concentrations of xenobiotic ions or metals (e.g., Au, Ag, Cd, Sn, Hg, Pb, etc.) by means of an active process (reductase/hydrogenase enzymes) or a passive process (metallothioneins) (Bertini et al. 2007). In each of these examples, processes may be mediated by various types of resistance mechanisms encoded by plasmids (or transposons) that can be activated not only in their offspring but also in other bacteria of the same or different species, triggering the mobilization of enzymatic pathways in order to initiate detoxification and maintain survival (Rai and Duran 2011; Rouch et al. 1995). Consequently, nanotechnology has used these pathways in order to bioreduce metal ions to form more stable metal particles (Beveridge et al. 1996; Carpentier et al. 2003; Rouch et al. 1995; Silver 1996) (Fig. 5).

These mechanisms include efflux systems and alterations in solubility and toxicity due to changes in the redox state of metal ions, complexation and chelation reactions, precipitation of metals either extracellularly or intracellularly or in the periplasmic space, and the lack of specific systems for transport of metals (Carpentier et al. 2003; Rai and Duran 2011). In 2005, Oleg A. Zadvorny and collaborators (Zadvorny et al. 2005) demonstrated that two phototrophic purple sulfur bacteria (PSB) (*Thiocapsa roseopersicina* and *Lamprobacter modestohalophilus*) can reduce Ni (II), Pt (IV), and Pd (II) due to the action of hydrogenase with an electron donor. These hydrogenases have valuable theoretical and practical utility as a type of "metal oxidoreductase." Thus, by 2006 Maggy F. Lengke et al. (Lengke et al. 2006) were already offering the first viable alternative method to standard chemical methods for developing Pt nanoparticles. In this study, the synthesis of Pt nanoparticles by interacting platinum (IV) chloride $\left(PtCl_4\right)$ with a filamentous cyanobacterium from the species *Plectonema boryanum* (UTEX 485 strain) was investigated in order to react and precipitate these as amorphous spherical nanoparticles (≤0.3 μm), both intracellularly and extracellularly. The presence of intracellular platinum suggested that platinum entered the cells as $PtCl_4$ and, according to complementary analyses, the Pt (IV) complex was reduced to Pt (II) and then to Pt (0) due to its interaction with sulfur, phosphorus, and nitrogen, They thus deduced a staged reaction as shown below (Brayner et al. 2007; Lengke et al. 2006):

$$\mathrm{Pt(IV)}\left[\mathrm{PtCl}_{4(\mathrm{ac})}\right] \rightarrow \mathrm{Pt\ (II)}\left[\mathrm{Pt\ (II)-organics}\right] \rightarrow \mathrm{Pt(0)} \quad (1)$$

where Pt (II) forms a type of organometallic complex, although this is still not very clear. However, three years later they proposed, with experimental evidence based on an uncharacterized consortium of sulfate-reducing bacteria (SRB), a two-stage enzymatic process for the bioreduction of Pt (IV) to Pt (0) by means of hydrogenases with interference from two electrons (Riddin et al. 2009).

$$2\mathrm{H}^{+}2\mathrm{e}^{-} \xrightarrow{\text{hydrogenase}} \mathrm{H}_2; E^0 = 0\ \mathrm{eV} \quad (2)$$

The first "fast" stage from Pt (IV) to Pt (II) occurred in the cytoplasm through a hydrogenase redox system, whereas Pt (II) begins the second stage in a "slow" way, diffusing into the periplasm and then reducing to Pt (0) (Govender et al. 2009; Siddiqi and Husen 2016):

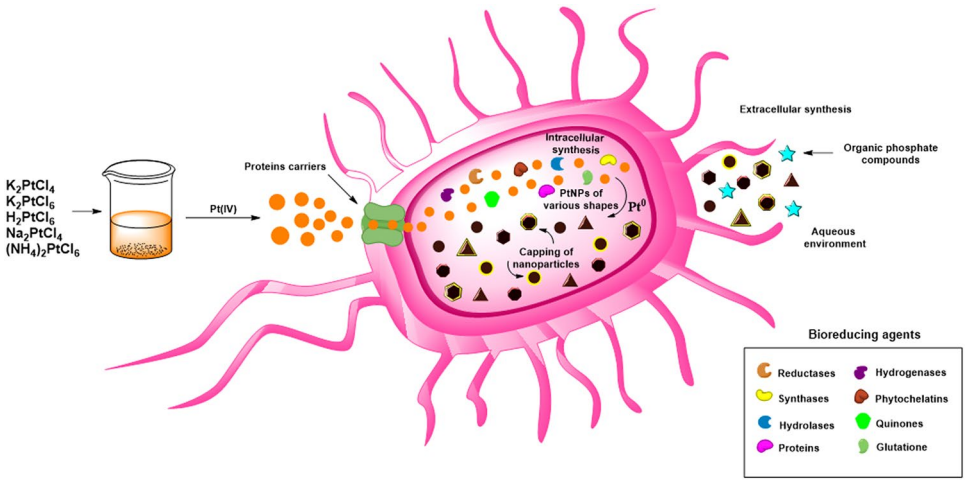

Fig. 5. Extracellular and intracellular bacterial synthesis of nanoparticles (adapted from Bloch et al. 2021)

$$Pt^{4+} \xrightarrow{2e^-} Pt^{2+} \xrightarrow{2e^-} Pt^0 \quad (3)$$

by one or more oxygen-sensitive periplasmic hydrogenase. However, this mechanism remains debatable and will be clarified by greater understanding of the platinum bioreduction mechanism (Govender et al. 2010).

Furthermore, this finding confirms the studies and hypotheses proposed in 2007 by two research groups involving hydrogenase enzymes and reducing bacteria, *Shewanella algae* and a mixed consortium of SRB, respectively, where it was demonstrated that the platinum salts were bioreduced and the metallic Pt deposited in the periplasm (Konishi et al. 2007; Rashamuse and Whiteley 2007). Additionally, unlike Zadvorny et al. (2005), in the research of Riddin et al. (2009) Pt (IV) ions were shown to bioreduce to Pt (0) in the presence or absence of an exogenous electron donor, while Zadvorny only used an electron donor (methyl viologen). In 2008, the potential of the purified enzyme to recover platinum from wastewater was investigated, demonstrating the industry application (Rashamuse, et al. 2008). Riddin et al. (2010) show that, like chemical syntheses, the concentration of platinum salt and proteins plays an important role in the control of size and shape, as their previous studies showed that when using only cells, amorphous deposits of Pt (0) were obtained, but when the cells are eliminated with variations of salt and protein extracts, the morphology of the nanoparticles may vary (Riddin et al. 2009; Brayner et al. 2007).

To date, researchers have relied primarily on known freshwater bacteria and very little research has focused on other bacteria. Five years ago, however, Maes et al. (2016) showed a radical change when using halophilic bacterial cultures from the Halomonadaceae, Bacillaceae, and Idiomarinaceae families, which managed to recover > 98% of Pt (II) and > 97% of Pt (IV) at pH 2 over a period of between 3 and 21 hours $\left(453\ \text{mg}\ Pt_{\text{recovered}}\ h^{-1}g^{-1}\text{biomass}\right)$ from solutions of $K_2Pt(II)Cl_4$ and $K_2Pt(IV)Cl_6$ at 100 mg L^{-1}. Based on previous studies, we can better select the microorganisms to be adapted to industrial conditions that we require today, as not all bacteria are able to reduce platinum (Konishi et al. 2007; Maes et al. 2016; Yong et al. 2002).

Baskaran et al. proposed a mechanism for the extracellular production of Pt nanoparticles in *Streptomyces sp*. The chloride reductase enzyme is involved in the nitrogen cycle and is responsible for the reduction of chloride to chlorine. The nicotinamide adenine dinucleotide-dependent chloride reductase enzyme is known to be an important factor in the biogenic synthesis of nanoparticles. A possible mechanism is the electron shuttle enzymatic metal reduction process (Baskaran et al. 2017):

$$\begin{aligned} &C_{21}H_{27}N_7O_{14}P_2 + K_2PtCl_6 + 29O_2 \\ &\quad \rightarrow 21CO_2 \uparrow + 7NO_2 \uparrow + 2H_3PO_4 + 6HCl \\ &\quad + 2KOH + Pt \downarrow + 6H_2O + \frac{1}{2}H_2(\uparrow) \end{aligned} \quad (4)$$

Due to their ability to reduce metals, sulfate-reducing bacteria are not only used to remove toxic metals but also for the biogenic synthesis of platinum nanoparticles in which the *Acinetobacter calcoaceticus* and *Desulfovibrio vulgaris* strains have been used (Gaidhani et al. 2014; Martins et al. 2017).

Synthesis mediated by other microorganisms or substances

As observed in the previous sections, protocols have been developed to obtain monodispersed and stable platinum nanoparticles by bio-synthetic methods, where derivatives of plants, bacteria, and fungi are the main promoters of platinum nanoparticle synthesis. However, there are other methods using biogenic elements.

One of the first reports on the use of elements of this nature was made by Nadagouda and Varma (2006), who used one of the most frequent organic cofactors in nature, vitamin B2, with a density-assisted self-assembly method in different solvent media. Additionally, obtaining platinum nanoparticles without the intervention of reducing agents in the system to transform the precursor of platinum is being considered—something that many end up happening even with the use of friendly materials (Cai et al. 2009; Deng et al. 2009). Benaissi et al. (2010) used cotton nanocrystalline cellulose alone to do all the reduction and stabilization work, thanks to the functional groups at the surface of the biopolymer. It is well known that cellulose (Benaissi et al. 2010), lignin (Coccia et al. 2012), and hemicelluloses (Lin et al. 2016) are the main constituents of the cell wall in plants, so wood becomes interesting due to the electron-rich nature of hydroxyl and ether groups, which can act as high-speed reducers of metal ions that are suitable for the preparation of Pt nanoparticles (Lin et al. 2011). However, we can also find other interesting derivatives such as fulvic acid (Coccia et al. 2012), humic extract, and bacterial cellulose matrixes (Aritonang et al. 2014). Information about biogenic substances is accumulating slowly, but safe approaches are being worked on, as these do not require toxic reagents to obtain this material, thus preventing the release of toxic substances that may play an important role in the immune system. This has led to more complex substances such as sheep's milk, quail egg yolk, and honey being used in an attempt to maintain mild conditions (Gholami-Shabani et al. 2016; Nadaroglu et al. 2017; Venu et al. 2011). These are often used as a mixture of simultaneous reducing and stabilizing agents. In this

sense, the bio-manufacture of these elements is developing as a modern and appropriate technique for improving the shape, size, and stability of Pt nanoparticles with the help of techniques that are apt for clarifying their nanoscopic levels (Jeyaraj et al. 2019). Because these are new synthetic strategies, work to establish training mechanisms has been limited. However, these techniques are particularly useful, as by using renewable resources of this type one saves on independent reducing and stabilizing agents. But applications continue to be focused on catalysis, neglecting the possible applications related to anticancer, antimicrobial, and antifungal activity.

Conclusion

All these synthetic strategies reveal an effort to improve the ecological conditions that surround us by using less toxic synthesis methods. These constructive syntheses are controlled by the platinum precursor, temperature, and use of reagents or organisms that will affect the shape and size of the platinum nanoparticles, playing a decisive role in safety and in producing successful applications in the biomedical context. Due to the complexity of the biological environment, where each organism produces materials that result in a corresponding reaction, devising a universal strategy seems unlikely. However, results still show discrepancies. Thus, platinum nanoparticles are undergoing rigorous nanotoxicological investigations with the aim of outperforming their more commonly available analogs (nickel, gold, silver, iron oxide, gadolinium, and titanium dioxide) and their predecessors (cisplatin, carboplatin, oxaliplatin, etc.), demonstrating an improved cytotoxic and pharmacokinetic profile (Almarzoug et al. 2020; Gurunathan et al. 2020, 2019; Kankala et al. 2020; Labrador-Rached et al. 2018; Ma et al. 2019; Shatokhina et al. 2020; Zhang et al. 2018).

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Declarations

Conflict of interest The authors declare no conflict of interest.

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