Journal of Chemical Health Risks

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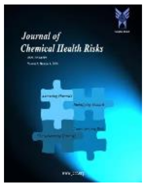
JCHR (2023) 13(6), 1421-1431 | ISSN:2251-6727



A Review on the Biosynthesis of Metallic Nanoparticles: In Respect of Characterization and Therapeutic Application

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(Received: 07 October 2023 Revised: 12 November Accepted: 06 December)

KEYWORDS

Biosynthesis; nanotechnology; green chemistry; biosorption; plant biotechnology

ABSTRACT:

Introduction: Nanoparticles exhibit unique properties that enable them to find potential applications in various fields. Accordingly, significant research attention is being given to the development of novel strategies for the synthesis of nanoparticles. Among these, biological route of nanoparticle synthesis has been portrayed as an efficient, low-cost and environmentally friendly technique. Biological materials such as bacteria, fungi, yeast, algae and plant have been reported to possess high bio reduction ability to synthesize various size and shape of metallic nanoparticles.

Objectives: Of these biomaterials, this review focuses on plant-mediated biosynthesis of metallic nanoparticles.

Methods: There are two basic approaches to attain nanostructures, viz. top-down and bottom-up methods. Top-down approach involves break down of bulk material into fine particles through size reduction using various lithographic techniques e.g., grinding, milling, sputtering and thermal/laser ablation

Results: Due to their unique properties, nanoparticles are widely used in different fields such as medicine, agriculture, cosmetic industry, drug delivery, catalysis and wastewater treatment.

Conclusions: Due to their unique properties, nanoparticles are widely used in different fields such as medicine, agriculture, cosmetic industry, drug delivery, catalysis and wastewater treatment. Figure 8 illustrate applications of nanoparticles in various fields. In particular, biosynthesized metallic nanoparticles are much preferred especially in medical-based applications.

1. Introduction

Nanoscience is a multidisciplinary field that involves the design and engineering of functional systems at the molecular scale. It is a field of applied science focused on the synthesis, characterization and application of materials and devices on the nanoscale. In general, nanoscience can be defined as the art and science of manipulating matter at the nanoscale to create new and unique materials. Nanoscale materials are usually categorized as materials having structured components with at least one dimension less than 100 nm. The emergence of nanoscience has provided promising results in recent years by intersecting with various other branches of science and forming impact on all forms of life. There are two basic approaches to attain nanostructures, viz. top-down and bottom-up methods [1]. Top-down approach involves break down of bulk material into fine particles through size reduction using various lithographic techniques e.g., grinding, milling, sputtering and thermal/laser ablation [2]. In bottom-up approach, the nanoparticles are fabricated from smaller entities, for example by joining atoms, molecules and smaller particles [3]. The bottom-up synthesis mostly relies on chemical and biological methods of production. An important benefit of bottom-up approach is the increased possibility of preparing metallic nanoparticles with relatively lesser defects and more homogeneous chemical composition [4]. Nanoparticles are of great interest owing to their extremely small size and high surface to volume ratio, which alter their physical and chemical properties (such as mechanical properties, biological and satirical properties, catalytic activity, thermal and electrical conductivity, optical absorption and melting point) compared to bulk of the same chemical composition [5].

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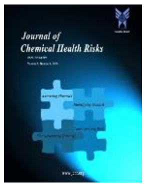

2. Objectives

Nanoparticles exhibit unique properties that enable them to find potential applications in various fields. Accordingly, significant research attention is being given to the development of novel strategies for the synthesis of nanoparticles. Among these, biological route of nanoparticle synthesis has been portrayed as an efficient, low-cost and environmentally friendly technique. Biological materials such as bacteria, fungi, yeast, algae and plant have been reported to possess high bio reduction ability to synthesize various size and shape of metallic nanoparticles. Of these biomaterials, this review focuses on plant-mediated biosynthesis of metallic nanoparticles. The biomolecules present in the plants such as terpenoids, flavones, ketones, aldehydes, proteins, amino acids, vitamins, alkaloids, tannins, phenolics, saponins, and polysaccharides play a vital role in reduction of metals.

3. Methods

3.1. Physical methods

Physical methods for synthesis of metallic nanoparticles include evaporation condensation, laser ablation, electrolysis, diffusion, plasma arcing, sputter deposition, pyrolysis and high energy ball milling [5]. Evaporation-condensation is generally carried out using a tube furnace at atmospheric pressure. The source material within a boat centred at the furnace is vaporized into a carrier gas. Nanoparticles of various materials such as Ag, Au and indium tin oxide (In2O5Sn) have been synthesised using evaporation-condensation technique [22]. However, synthesis of nanoparticles using a tube furnace at atmospheric pressure has some disadvantages; for example, tube furnace occupies a large space, consumes a great amount of energy while raising the environmental temperature around the source material, and requires a lot of time to achieve thermal stability [23]. The laser ablation method is typically designed to produce colloidal nanoparticles in a variety of solvents. The pulse laser ablation process takes place in the chamber under vacuum and in the presence of some inert gases [24

3.2. Chemical methods

Chemical methods for synthesis of nanoparticles include chemical reduction, microemulsion/colloidal, electrochemical and thermal decomposition. Chemical reduction by inorganic and organic reducing agents is one of the most common methods to synthesize colloidal metal particles because of ease in operation and equipment needed. Commonly used reducing agents are sodium borohydride (NaBH4) [27], potassium bitartrate (KC4H5O6) [28], methoxy polyethylene glycol (CH3O(CH2CH2O) nH) [29], trisodium citrate dihydrate (Na3C6H9O9) [30], ascorbate [5] and elemental hydrogen [31]. The aforementioned chemical agents reduce metallic ions and lead to the formation of corresponding metallic nanoparticles, which is followed by agglomeration into oligomeric clusters. Turkevich et al. [32] described for the first time the reduction of Au (III) ions to Au (0) using citric acid and further suggested that the method can also be stabilized to form monodispersed nanoparticles and could be exchanged to other ligand. Subsequently in 1994

3.3. Biological methods

In an attempt to develop low-cost and eco-friendly route, researchers have utilized the potential of biological materials for the synthesis of metallic nanoparticles. Biological (green) synthesis involves the reduction of metal ions using biological mass/extract as a source of reductants either extra-cellularly or intra-cellularly. Apart from cost-effectiveness and Eco friendliness, the advantages of biological approach over traditional physical and chemical methods include effectiveness of the process to catalyze reactions in aqueous media at standard temperature and pressure as well as flexibility of the process as it can be implemented in nearly any setting and at any scale [42]. The constituents of biological materials are responsible for reduction and the process is often triggered by several compounds present in the cell such as phenolic, carbonyl, amine, amide groups, proteins, 8 pigments, flavanones, terpenoids, alkaloids and other reducing agents [43

3.3. Plant-mediated biosynthesis of nanoparticles

For biosynthesis of nanoparticles, plants can be used in their live form or dead/inactive form. Several plants are known for their metal accumulation property and these accumulated metals later reduce to nanoparticles intra-cellularly [79]. Gold nanoparticles with a size range of 2 – 20 nm have been synthesized using the live alfalfa plants [80]. Bali and Harris [81] observed that metallophytes (Brassica juncea and Medicago sativa) initially accumulated Au from aqueous KAuCl4 solution and later stored Au as nanoparticles throughout the epidermis, cortex and vascular tissue of both species. The authors also determined the particle sizes ranged between 2 nm - 2 μm in B. juncea and 2 nm - 1 μm in M. sativa. However, recently much work has been done using inactive plant parts as reductant for synthesis of nanoparticles

3.4. Silver nanoparticles

Of all the metals, Ag has been studied extensively for plant-mediated biosynthesis and it proved easier and more rapid method than the tedious and time-consuming microbial synthesis processes [92]. Furthermore, synthesis of Ag nanoparticles is of much interest to the scientific community because of their wide range of applications including spectrally selective coating for solar energy absorption [93], surface enhanced Raman scattering for image [94] and many other biomedical applications [42]. Several plants and their

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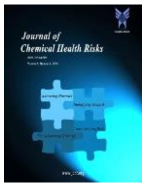

respective portions had been utilized for the preparation of Ag nanoparticles. Table 1 lists some of the important results of plant-mediated biosynthesis of Ag nanoparticles. Plant biosynthesis basically involves contacting silver nitrate salt ($AgNO_3$) with extract/biomass of plants. The appearance of brownish yellow colour after short span of contact confirms the formation of Ag nanoparticles according to the following reaction:

$Ag^+NO_3^-$ + Plant molecule (OH, C=H, etc.) → Ag^0 nanoparticles (1)

3.5. Gold nanoparticles

Gold nanoparticle also attracted several researchers in the field of plant-mediated biosynthesis owing to their unique properties and applications in nanoelectronics, biomedical, nonlinear optics, nanodevices and catalysis [99]. In particular, Au nanoparticles provide promising scaffolds for drug and gene delivery [100]. Their unique features such as tuneable core size, monodispersed, large surface to volume ratio, and easy functionalization with virtually any molecule or biomolecule allow targeting, transport, and tuning of delivery processes [101]. In general, bio reduction of chloroauric acid ($HAuCl_4$) to Au nanoparticles follows the below reaction

$H^+Au^{3+}4Cl^-.4H_2O$ + Plant molecule (OH, COOH, etc.) → Au^0 nanoparticles (2)

3.6. Platinum nanoparticles:

Platinum nanoparticles are widely used as catalysts as well as in many biomedical applications [92]. Compared to Ag and Au, the reports on Pt nanoparticles are significantly limited. The interaction between platinum solution and plant biomass usually leads to the following reaction:

$H_2Pt^+ 6Cl^- .6H_2O$ + Plant molecule (OH, COOH, etc.) → Pt^0 nanoparticles (3)

3.7. Palladium nanoparticles

Palladium nanoparticles are widely used as catalysts in various reactions and plasmonic wave guiding as well in chemoreceptor-type sensing devices [42]. The reduction of palladium chloride ($PdCl_2$) to nanoparticles by plant biomass follows the below equation:

$Pd^+Cl_2^-$ + Plant molecule (–C=C, –C=O, etc.) → Pd^0 nanoparticles (4)

4.Results

Characterization of plant-mediated biosynthesis of nanoparticles

Nanoparticles are typically characterized by their size, shape, surface area and dispersity nature. The common techniques of characterizing nanoparticles are as follows: UV–visible spectrophotometry, Fourier transform infrared spectroscopy (FTIR), powder Xray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM).

4.1. UV–visible spectrophotometry

The formation of various metallic nanoparticles from their respective metallic salts gives characteristic peaks at different absorptions that can be monitored using UV-visible spectrophotometry. In particular, noble metallic nanoparticles such as Ag and Au possess strong absorption in the visible region with the maximum in the range of 400 - 450 nm and 500 - 550 nm, respectively, due to the surface plasmon resonance (SPR) phenomenon which occurs in metallic nanoparticles [126].

4.2. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a surface chemical analytical technique, which measures the infrared intensity versus wavenumber (wavelength) of light. The nature of the functional groups and their involvement during bioreduction can be approximately evaluated using the FTIR spectroscopy.

4.3. X-ray diffraction (XRD)

The X-ray diffraction (XRD) technique is used to study structural information about crystalline metallic nanoparticle. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure [6]. If the nanoparticles are produced in an amorphous structure, no diffraction peak is observed and this technique cannot help to identify the sample [126].

4.4 Electron microscope

Scanning electron microscopy (SEM) provides information about the topography and morphology of the nanoparticles. In addition, electron microscopy techniques can also be used to measure the average size of nanoparticles using statistical software.

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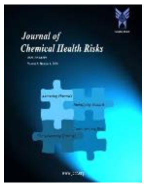

FACTORS INFLUENCING BIOSYNTHESIS OF NANOPARTICLES

Solution pH

The solution pH plays an important role in plant-mediated biosynthesis of nanoparticles. Several reports indicated that pH of the solution medium influences the size, shape and rate of the synthesized nanoparticles [147]. This phenomenon is due to the formation of nucleation centres, which increases with increase in pH. As the nucleation centre increases, the reduction of metallic ion to metal nanoparticles also increases.

Temperature

Temperature is another important factor that influences the size, shape and rate of nanoparticles. Similar to pH, formation of nucleation centres increases with increase in temperature, which in turn increase the rate of biosynthesis. Sneha et al. [59] studied the effect of temperature on biosynthesis of Au nanoparticles by Piper betle leaf extract. Through TEM images, the authors visualized mainly nanotriangles at 20 ○C, whereas nanoplatelets and nanoparticles ranging in size from 5 - 500 nm were observed at 30 – 40 ○C.

Reaction time

The size, shape and extent of nanoparticle synthesis using plant-based biomaterials also greatly influenced by the length of reaction time the suspension medium is incubated. Nazeruddin et al. [152] observed rapid synthesis of Ag nanoparticles by seed extract of Coriandrum sativum within 1 – 2 h as compared to 2 – 4 days required by microorganisms. Similarly, Noruzi et al. [87] reported that the Rosa hybrid petal mediated synthesis of Au nanoparticle's reaction was rapid and completed within 5 min.

Plant extract/biomass dosage

The concentration of plant biomass/extract often decides the efficiency of nanoparticle synthesis. Several investigators identified that increase in biomass dosage enhances the production of nanoparticles as well as alter the shape of nanoparticles [111,156]. Hence, it is often essential to determine optimum biomass dosage for the process. Chandran et al. [157] used the Aloe vera leaf extract to modulate the shape and the size of the synthesized Au nanoparticles.

4. Discussion

Due to their unique properties, nanoparticles are widely used in different fields such as medicine, agriculture, cosmetic industry, drug delivery, catalysis and wastewater treatment. Figure 8 illustrate applications of nanoparticles in various fields. In particular, biosynthesized metallic nanoparticles are much preferred especially in medical-based applications. The nanoparticles exhibit high differential uptake efficiency in the target cells over normal cells through preventing them from prematurely interacting with the biological environment, enhanced permeation and retention effect in disease tissues and improving their cellular uptake, resulting in decreased toxicity [158]. The use of nanoparticles for cancer therapy has been gaining popularity in recent years. Several researchers explored the cytotoxic effects of various metallic nanoparticles on different cell lines synthesized using plant biomass/extracts [139, 145, 159]. Raghunandan et al. [160] synthesized Au and Ag nanoparticles using guava and clove plant extracts and subsequently examined their anticancer efficacy against different cancer cell lines including human colorectal adenocarcinoma, human kidney, human chronic myelogenous, leukaemia, bone marrow, and human cervix

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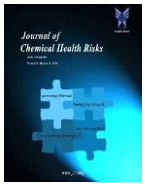

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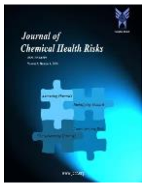

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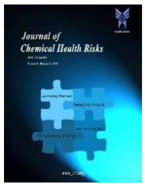

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