Toxicological Impacts of Biogenic Vs. Conventional Metal Nanoparticles: Safety Perspectives and Emerging Trends

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Abstract

Although nanoparticles (NPs) have transformed a number of industries, including environmental cleanup and medicine, there are still serious concerns about their safety. This review highlights the effects of conventional and biogenic metal nanoparticles on the environment and human health by analyzing their toxicological profiles. Because of their environmentally benign synthesis and biocompatibility, biogenic nanoparticles which are produced utilizing biological entities like plants, bacteria, or fungi are frequently seen as safer. On the other hand, due to little size, enhanced surface, and residual chemical reagents, ordinary metal nanoparticles that are created by physical or chemical means may be more harmful. Analysis is done on the main mechanisms of toxicity caused by nanoparticles, such as oxidative stress, genotoxicity, and inflammatory reactions. To reduce toxicity, recent developments in the sector have focused on hybrid nanoparticles, surface functionalization, and green production techniques. The analysis examines regulatory structures and challenges in uniform safety evaluations for biogenic nanoparticles, highlighting their potential for safer applications but also highlighting significant obstacles to their scalability and reproducibility. This work underscores the importance of cross-disciplinary approaches that balance innovation and safety to ensure responsible nanotechnology deployment in the future.

Keywords: Nanoparticles, Biogenic, Conventional, Metal nanoparticles, Safety perspectives

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Introduction

Nanoparticles are tiny particles with sizes between 10 and 1000 nm. Drugs can be mixed into, trapped inside, coated onto, or attached to these particles. Depending on how they are made, the particles can be of different types like nanospheres (solid particles with the drug spread throughout) or nanocapsules (tiny capsules with the drug inside) (Langer, 2000). The fabrication of nanoparticles with sizes stretch from 1 to 100 nm using various synthesis techniques, as well as the alteration of particle size and structure, is the field of nanotechnology. These days, Nanoparticles are being used more and more in many fields, such as biology, physics, chemistry, medicine, and material science (Heiligtag & Niederberger, 2013) . Particles of bigger bulk material do not exhibit the unique and enhanced characteristics of nanoparticle size reduction, such as, form and size distribution of fine particles (Willems, 2005). The term 'nanoparticle,' is derived from the Greek word 'nano,' meaning 'dwarf or small' A nanoparticle is a particle with one dimension in the size range of 10-9, and 1 nm is equivalent one billionth of a meter (You et al., 2013).

Metallic nanoparticles are often made and stabilized using methods like electrochemical changes, chemical reduction, and photochemical reduction (Chen et al., 2001). The method chosen to make metallic nanoparticles are equally important because their morphology (size and structure), stability and properties of metallic nanoparticles depend on factors like how metal ions react with reducing agents, how stabilizing agents interact with the nanoparticles, and the methods used during their production (Vijayakumar et al., 2013). In many studies on the creation and use of nanoparticles of diverse inorganic metal (silver, gold, copper, iron, platinum, and palladium), scientists have demonstrated their proficiency in metallic nanoparticles, which are currently the focus of much of their research (Azharuddin et al., 2019).

Deposition, sputtering, ball milling, and plasma-based methods are the physical methods to develop nanomaterials (Dhand et al., 2015). Laser and plasma ablation, laser ablation and plasma techniques demand a high energy input. The majority of physical processes are too costly to be used in practical business use due to their range of size distribution, sluggish production rate, waste byproducts, and large energy usage (Seetharaman et al., 2018).

The majority of the chemical approaches that have been proposed for the preparation of nanoparticles such as chemical reduction, pyrolysis, sol-gel, microemulsion, polyol synthesis, hydrothermal synthesis, and chemical vapour deposition are commonly employed to create nanostructured materials (Darroudi et al., 2013). Furthermore, it is fatal for both persons and the environment to use dangerous chemicals and reagents during the compounding process and byproduct formation (Zhang et al., 2019). This can be considered as a reason why these NPs are not so often employed in biological fields.

Green nanotechnology is a relatively newly developing area of science and engineering that designs new NPs throughout the concept of green chemistry. Synthesis of proteins and enzymes, with natural stabilising and reducing elements, introduces yet another innovative package of biological techniques in the creation of NPs. It is also economical and safe for the environment apart from chemophysical procedures because it lacks any poisonous content (Patil et al., 2020). The bio synthesis of NPs is a bottom up approach that involves utilizing simple single celled to complex multicellular organisms inclusive of bacteria, fungus, actinomycetes, yeast, algae and plant material (Kalishwaralal et al., 2010).

The synthesis and manufacturing of nanoparticles should be easy even though green nanoparticles appear to be an innovative method of developing conventional nanoparticles. Microbes and plants were the bio-resources to be exact available in the universe. However, the use of such bioresources is essential from the standpoint of synthesis and commercialization. In this situation, microorganisms can be used efficiently; however, the synthesis and use of nanoparticles are hampered by the dealing with microbes, increasing production, genetic changes, issues in large-scale growth, processing, and other factors (Patil et al., 2020).

Methods Involve for the Synthesis of Nanoparticles

Following two types of methods are involved in the preparation of nanoparticles:

1. Conventional nanoparticles synthesis
2. Biological-mediated synthesis of nanoparticles

Conventional Nanoparticles Synthesis

Conventional synthesis of nanoparticles two types of processes:

1. Physical Methods of Nanoparticles Synthesis

Physical synthesis of nanoparticles involves following methods:

Ball Milling

Using high intensity ball milling to reduce particle size is the fundamental principle of mechanical milling. The characteristics of mechanical milling depend on the type of powder and the process variables. It is divided into two categories: high energy and low energy milling, which rely on the powder mixture's induced mechanical energy. The most common method for producing nanosized particles is high intensity ball milling (Rajput & Technology, 2015). In this procedure the following numbers of heavy balls are added to a container along with the bulk powder. The second step is the fast spinning of the mixed powder so as to apply force energy on it is achieved. These high-energy mills are attrition ball mills, planetary ball mills, vibrating ball mills, low-energy tumble mills, high-energy ball mills, and more that can reduce the particle size (Rajput & Technology, 2015).

Ion Sputtering

Using an ion beam of inert gas, a solid can be vaporised using the ion sputtering technique. In recent years, some metals have been employed to synthesize nanoparticles employing magnetron sputtering of metal objectives. At relatively low pressures (1 mTorr), the complete process is carried out (Swihart & science, 2003). The process of sputter deposition takes place in an evacuated vacuum chamber with a working pressure of, say, 0.05 and 0.1 mbar, with sputtering gas allowed. In a magnetic control method, a very high voltage is applied to the target (cathode) in a spiralling motion of electrons. This ionises the gas as the sputtering argon atoms are met. This continuous process forms a glow discharge, or plasma, which ignites. The target is attracted to the ball of glowing and positively charged gas ions which keep on hitting it. When this recurs and approaches the target's surface, the gas molecules bombard metal atoms in vacuum and knock the atoms off randomly leaving a cloud on the surface possessing energy exceeding the binding energy, which leads to expulsion of an atom (Vanecht, 2012).

Laser Ablation

By employing laser light the laser ablation method is one which decreases the particle size to the nanoscale. Subsequently, the solid target material coated so that it is thinly coated is irradiated by pulsed laser light. Nd:YAG (neodymium-doped yttrium aluminium garnet) laser at 106 µm output and its harmonic, copper vapour laser, and Ti:Sapphire (titanium-doped sapphire) laser are the main lasers used (Simakin et al., 2004). A material exposed to laser light breaks up into tiny particles known as the nanoparticles. These particles are deposited in the liquid that surrounds the target thereby forming a colloidal solution. The power density and the pulse width define the yield of ablated atoms and particles formed in proportion (Kruis et al., 1998). Several important factors affecting ablation efficiency and the properties of metal particles include laser pulse width, wavelength, ablation period, laser density, along with an effective surrounding liquid media with or without surfactant (Abou El-Nour et al., 2010).

Physical Vapor Deposition

Material is deposited on a surface via the physical accumulation process in the form of nanoparticles or thin films. Material vaporises when subjected to highly regulated vacuum techniques like thermal evaporation and sputtered deposition, and then condenses on a substrate (Pandey et al., 2011). Lanthanum strontium cobalt thin films are typically synthesized using physical vapour deposition methods such pulsed vapour deposition (Park et al., 2017). In pulsed laser deposition, a solid target is hit by a laser, causing it to release a plasma of particles. These particles are then deposited onto a substrate to form a film (Gondoni et al., 2013). This method is commonly used for depositing thin films and metal nanoparticles, especially for carbon nanotubes (Pandey et al., 2011).

2. Chemical-mediated Synthesis of Nanoparticles

Chemical synthesis of nanoparticles involves following methods:

Sol gel Method

Two phases make up the sol gel method of creating nanoparticles: either a) the merging of metal and metal oxide or nanoparticles directly into a prehydrolyzed sol of silica or b) the mixing of preformed colloidal metal (oxide) and a sol which contains the matrix forming species after which gelation takes place. Before hydrolysis, metals reduce and form a complex with silone (Cushing et al., 2004). This method forms a coated gel in the continuum of liquid phase gelatin-matrix colloidal suspension sol. Cationic metal alkoxide and/or aloxysilane is employed as an initiator in colloid synthesis. The two most often used tetramethoxysilanes (TMS) and tetraethoxysilanes to create silica gel. Metal alkoxides are immiscible in water and are the organo-metallic precursors of many different metals, including titanium, aluminium, and silica. Alcohol serves as a reciprocal solvent. It starts a reaction at a fixed pH by incorporating a catalyst within a homogeneous medium of one or more preferred alkoxides. Four significant processes involved in sol-gel are hydrolysis, condensation, particle growth, and particle coagulation (Rajput & Technology, 2015). Low temperature heat treatment is utilized in deposition of metal oxide particles in direct precipitation of metal/ metal oxide from silica sol process and thin film preparation is the predominate use for this method (Cushing et al., 2004).

Chemical Reduction

Using chemical reduction technique, several reducing agents are used when a surfactant is present to reduce ionic salt in the correct medium (Guzmán et al., 2009). Metal nanoparticles are formed in aqueous solution by the use of sodium borohydride or another reducing agent. Lai and Mohanty used trisodium citrate (TSC) or sodium lauryl sulphate (SLS) to cap the metal nanoparticles that are formed. At times these two stabilising and reducing agents are combined in one formula. The stability of the metal nanoparticles in the dispersion was measured by the absorbance study (Chattopadhyay & Patel, 2014). Otherwise known as sodium borohydrate ($NaBH_4$), glucose, ethylene glycol, ethanol, sodium citrate and hydrazine hydrate are used to synthesise silver nanoparticles (Landage et al., 2014).

Hydrothermal Method

Vapours from an aqueous solution interact with a solid to form small particle deposition in the hydrothermal process at elevated temperatures and pressures. In doing so, the cations function as polymeric hydroxide, which promote dehydration of the material a step at a time and thus facilitate the completion of the metal oxide crystal structure. The second metal cation that forms when base is added to the metal salt solution also reduces the formation of complex hydroxide prevents the formation of large number of particles and thus controls the particle generation process (Tavakoli et al., 2007).

Flame Pyrolysis

Flame pyrolysis works by first-hand spraying a liquid precursor into a flame, which forms nanostructures. Initiators with insufficiently high vapour pressure can be delivered in the form of vapour using this technique (Mädler et al., 2002). The precursor is exposed to the flame, allowing it to form nanoparticles as gases (vapor-fed aerosol flame synthesis), liquid (flame-assisted spray pyrolysis: FASP and flame spray pyrolysis: FSP), or solid (Wallace et al., 2013).

Biological-mediated Synthesis of Nanoparticles

There are two kind of naturally occurring biogenic metallic nanoparticle synthesis:

Bioreduction

Microbes and their enzymes convert metal ions into a stable form for biological processes. It is safe to remove the produced metallic nanostructures from adulterated material due to their inert and stable nature (Pantidos et al., 2014).

Biosorption

This novel approach to nanoparticle production involves allowing metal cations in aqueous media to attach to the cell wall of an organism, which in turn causes the development of stable nanoparticles through cell wall or peptide contact (Pantidos et al., 2014).

Nanoparticle Synthesis using Bacteria

Global interest in the suitable application of naturally available resources, like microorganisms, for the synthesis of nanoparticles is constantly growing. Since prokaryotes are abundant in the environment and can adjust to harsh conditions, they have gained attention as a way to make metallic nanoparticles. Some benefits of bacteria include their quick growth and convenience of cultivation and manipulation (Pantidos et al., 2014). Conditions such as temperature, duration of incubation, and oxygenation can be adjusted to influence the growth. According to (He et al., 2007) altering the growth medium's pH during incubation results in nanoparticles with varying sizes and shapes .

Nanoparticle Synthesis using Fungi

Fungi release enzymes and proteins that act as reducing agents to create metal nanoparticles from metal salts. Because of electrostatic contact, metals like silver (Ag) can bind to the cytoplasmic membrane and undergo reduction, which in turn generates silver nuclei and ultimately causes an deposition of both silver nuclei and nanoparticles. Popular fungi for creating nanoparticles include *Trichoderma reesei, Aspergillus fumigates, Fusarium oxysporum*, and others. The *Fusarium oxysporum* secretes reducing agents that effectively lower these metal ions. Because they require high aseptic conditions to be maintained, microorganism-based nanoparticle syntheses are not practically possible (Pantidos et al., 2014).

Nanoparticle Synthesis using Plant and plant Products

The world has lately expressed interest in the production of plant base nanoparticles (Prathna et al., 2011). The metallic nanoparticles include copper, zinc, silver and gold and these are synthesized with different plant parts and extracts. Secondary metabolites isolated from plants such as phenolic acid, flavonoids, terpenoid, alkaloid, and crude extracts are rich in compounds, which mainly reduce metallic ions to form metallic nanoparticles. Plant redox reactions using metabolic pathways employ both primary and secondary metabolites. These characteristics are applied as capping and reducing agents when synthesizing environment-friendly nanoparticles (Iravani, 2011; Kuppusamy et al., 2016) *Juncea brassica, Ilex crenata, Sesbania drummondii, Clethra barbinervis,* and *Acanthopanax scidophylloides* can advance photoremediation of heavy metals (Iravani, 2011). The bio-reducing agent is next removed from the biological extract and then mixed with aqueous solution of the metal precursor to generate nanoparticles. Spontaneous formation of nanosized particles is observed at room temperature during a number of processes. At times, due to synthesis time constraint, CD is added and heated, or at least, heated. Plant extracts are selected based on availability, ability to produce large quantities of the given extract and the waste produced in the process is ecologically nontoxic (Pantidos et al., 2014).

Safety Aspect \ Advantages

Conventional Method of Nanoparticles Synthesis

The advantages \safety aspects of conventional methods are as follow:

1. Beneficial for producing high-quality nanoparticles on a large scale at a reasonable cost, with improved solubility of therapeutic components that are indissoluble in water (Ullah et al., 2014; Thamizharasan et al., 2017).
2. It is feasible to produce nanoparticles in liquid media without the need to add surfactant (Simakin et al., 2004).
3. The material that is spat out has the same composition as the target material and is not changed (Kruis et al., 1998).
4. Superior approach compared to evaporation and laser ablation for refractory metals and intermetallic complexes.
5. A viable substitute gas-phase technique for producing metal oxide nanoparticles is flame pyrolysis.
6. It enhances the material's properties by optimizing its composition and grain size (Ullah et al., 2014).
7. The great film endurance of the chemical vapour deposition coating technique is demonstrated (Reina et al., 2009).
8. It is feasible to regulate particle size and shape through methodical observation of reaction parameters (Hasnidawani et al., 2016).
9. Nanoparticles can be prepared to the required size and shape (Tavakoli et al., 2007).
10. Powder that is well-crystallized can be produced.

Biogenic Method of Nanoparticles Synthesis

The advantages\safety aspects of biogenic methods are as follow:

1. Easily accessible and capable of withstanding harsh environments (Pantidos et al., 2014).
2. Not as pathogenic as bacteria and fungus.
3. The result is somewhat homogeneous nanoparticles (Pantidos et al., 2014).
4. Because of mycelia, nanoparticle synthesis has a huge surface area, is inexpensive, flexible, and easy to scale up for downstream processing.
5. Fungal secretions of proteins surpass those of bacteria in terms of productivity (Pantidos et al., 2014).
6. Non-toxic, environmentally friendly, and biocompatible
7. Toxic chemicals, high pressure, energy, and temperature are not used in green synthesis (Karnani & Chowdhary, 2013).

Toxicity \ Disadvantages

Conventional method of nanoparticles synthesis

The toxicity \ disadvantages of conventional methods are as follow:

1. Large amount of energy required.
2. Prolonged and extensive milling duration.
3. Powder contamination as a result of steel balls.
4. Extended laser ablation causes a large number of nanoparticles to develop in the colloidal solution, obstructing the laser's path and absorbing laser energy into the nanoparticles rather than the target surface. Overall, this causes the ablation rate to decrease (Ghorbani, 2014).
5. The sputtering gas (He, Ne, Ar, Kr, Xe) affects the surface features, composition, texture, and optical properties of nanocrystalline metal oxide films (Chandra et al., 2006).
6. Dangerous chemicals and the creation of harmful final goods
7. Participation in high-energy procedures
8. Process control is a challenging task.
9. Reliability and reproducibility are limited (Tavakoli et al., 2007).
10. Expensive

Biogenic Method of Nanoparticles Synthesis

The toxicity \ disadvantages of biogenic methods are as follow:

1. It can be difficult to precisely manage size and shape.
2. Scaling up can be difficult.
3. Biological sources can vary.
4. Green nanoparticles can penetrate cells and, above a certain limit, cause oxidative DNA damage, cell membrane harm, and disrupt the electron transport chain (Jamkhande et al., 2019).

Future Possibilities

Metal nanoparticles are increasingly used in fields like material science, physics, chemistry, and biology. Their synthesis involves various methods, such as sol-gel, chemical vapor deposition, physical vapor deposition, and green synthesis. Green synthesis is affordable, eco-friendly, sustainable, and free of harmful chemicals. However, more precise methods are needed for commercial applications (Jamkhande et al., 2019).

Conclusion

Nanoparticles hold immense potential across various fields due to their unique properties, with synthesis methods ranging from conventional chemical and physical approaches to green, biologically mediated techniques. While conventional methods offer scalability and control, they often involve high energy demands and hazardous chemicals, posing environmental and health risks. In contrast, biogenic synthesis is eco-friendly and biocompatible but faces challenges in scalability and uniformity. Green synthesis stands out as a promising, sustainable alternative, yet it requires further refinement to meet commercial demands. Balancing innovation, safety, and environmental responsibility is crucial for advancing nanoparticle applications in a sustainable future.

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