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Review Article

An Overview on Bioinspired Selenium Nanoparticles Synthesis Using Various Natural Sources with its Mechanism of Action.

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Abstract

Selenium is a vital micronutrient essential for the health of humans, animals, and microorganisms. Recently, there has been a growing interest among researchers in selenium nanoparticles (SeNPs) due to their biocompatibility, bioavailability, and low toxicity. The increased bioactivity of selenium nanoparticles has led to their widespread use in various biomedical applications. While selenium nanoparticles can be synthesized through physical, chemical, and biological methods, those biologically synthesized demonstrate greater compatibility with human organs and tissues with minimum tissue rejection. Researchers have extensively explored the impact of size, shape, and synthesis method on their applications in biological systems. This review covers various synthesis methods, highlighting biosynthesis over various physical methods.

Keywords: Top Down, Bottom Up, Ostwald Maturation, Selenocysteine and Bioinspired.

1. Introduction

Nanotechnology is a broad topic that deals with the design and engineering of practical systems at the molecular level. This multidisciplinary approach focuses on the separation, categorization, and application of resources and procedures at the nanoscale. Many substances are employed to expand as nanoparticles for beneficial effects. The world is currently at greater risk of limiting its natural resources, which in turn is harming agricultural development. These social stressors have led researchers to resort to nanotechnology, which offers a breakthrough in the various fields of medicine, agriculture, biotechnology, pesticides, and many more to provide immediate solutions [1]. The advancement in this field is increasingly contributing to the digitalization of agriculture through the rapid increase in the use of nano pesticides, nano fertilizers, nano biosensors, and many more [2]. The increasing usage of these nanomaterials has also met with some detrimental impacts concerning environmental health. The conventional synthesis of nanoparticles includes top-down as well as bottom-up approaches. Nanotechnology permits broad advances in agricultural research, agrochemicals that are conventionally used for crops by spraying or by broadcasting via certain nano-encapsulated agrochemicals that are planned in a way to acquire all the required properties like that of competent concentration, time-controlled release in the system in response to certain stimuli, enhanced targeted activity and easy mode of delivery. It has permitted broad advances in agricultural research, nano-encapsulated agrochemicals which are applied on crops by spraying or by broadcasting techniques [3].

1.1. Nanoparticle and Nanoparticle Synthesis

Nanomaterials in today's world are an active area of research. These are the natural or manufactured materials having a specific range of 1 and 100 nm, which is given by specific legislations in the European Union (EU) and the USA with specific references to the nanomaterials. They have a small size and a large surface-to-volume ratio which accounts for the prime reason for their uniqueness. Naturally occurring organic matter coated with organic components is widely used as a means of delivery for nanoparticles in plants. Natural nanomaterials are present on the surface of Earth's atmosphere regardless of human actions. Nanomaterials can be found in the oceans, lakes, soil, rocks, and even magma or lava at stages. The common nanoparticles include carbonaceous nanoparticles, organic nanoparticles, inorganic nanoparticles, and metal-based inorganic nanoparticles including silver (Ag), gold (Au) that have optoelectrical properties because of localized surface plasmon resonance (LPSR) characteristics and thus they find application in many research areas including agriculture and crop production. Carbonaceous nanoparticles which include fullerenes and nanotubes are representative of the two major classes of these carbonaceous nanoparticles. Researchers have shown increased commercial interest due to factors like high strength, electrical conductivity, and electron affinity [4]. Nanoscale zero-valent iron is a popular metallic nanoparticle in use for remediation of the environment and extensive study has shown that these nZVIs are being utilized for the removal of varied contaminants as these nZVIs depict high chemical reduction activity in the absence of oxygen [5]. Some other nanoparticles in use include lipid-based nanoparticles, and polymeric nanoparticles (PNPs) which are made from biocompatible and biodegradable polymers that are increasingly used for targeted drug delivery and the choice of the polymer and the ability to modify the drug release has made them ideal nanoparticles in use for the treatment of diseases like cancer. The common polymers used for the synthesis of these polymeric nanoparticles include chitosan, gelatin, and sodium alginate in addition to synthetic polymers like poly malic acid or polylactides. Semiconductor nanoparticles have both metallic and non-metallic properties which are being used in photocatalysis, electronic devices, and ceramic nanoparticles which are found in amorphous, dense, hollow, and many other forms [6].

1.2. Top-Down Synthesis

There are various methods for creating nanoparticles, and these approaches.

The destructive approach is used in this synthesis. The larger molecule (bulk material) decomposes into smaller molecules, which then turn into nanoparticles. Top-down synthesis is demonstrated by grinding or milling, physical vapour deposition, and other damaging methods [7].

2. Bottom-Up Methods

Bottom-up methods are sometimes referred to as constructive methods. It is the reverse of the top-down approach. Nanoparticles are created using this process from relatively simple ingredients. Chemical vapour deposition (CVD), sol-gel, spinning, pyrolysis, and biological synthesis are all examples of bottom-up methods [8].

2.1. Biological Synthesis

The manufacture of nanoparticles using plant extract and microorganisms such as bacteria and fungi is known as biological synthesis.

2.2. Selenium and Selenium Nanoparticle

Selenium occurs in two forms in nature: inorganic (selenite and selenate) and organic (selenomethionine and selenocysteine). Selenium can be found in nature in both crystalline and amorphous polymorphism forms. The crystalline forms of selenium are monoclinic and trigonal. Monoclinic selenium (m-Se) is red and contains Se8 rings. It appears in three allotropic forms based on distinct packings. At room temperature, trigonal selenium (t-Se) is the most stable crystalline form. Non-crystalline forms of selenium include red amorphous (a-Se), black amorphous, and vitreous selenium [9]. Selenium, which is found in selenoproteins and selenocompounds in the human body, is essential for reproduction, DNA synthesis, thyroid hormone production, metabolism, and defence against infections and oxidative damage. It has various industrial and commercial applications. It has excellent catalytic activity in organic hydration and oxidation reactions because to its high photoconductivity and low melting point [10]. The United Kingdom organisation of vitamins and minerals suggested that women and men consume 60 μg and 70 μg of selenium daily, respectively. A daily intake of more over 400 g may be harmful, resulting in a condition known as selenosis. Selenium is an important biochemical component of glutathione peroxidase, an enzyme that protects crucial SH-groups and decomposes peroxides, so functioning as an antioxidant [11].

Metal nanoparticles have an infinite number of uses in biomedicine thanks to the current growth in nanotechnology. Metal nanoparticles (Au and Ag) have enormous medical benefits but are more expensive to synthesise, whereas Se nanoparticles (SeNPs) are less expensive to synthesise and can be combined with other biological agents to enhance their biological features. SeNPs and lysozymes have a synergistic antibacterial action, according to due to their greater surface-to-volume ratio at the nano-level, the surface of the particles is more exposed, resulting in more deep selenium activity in the nano-regime [12]. In biological applications, SeNPs show promising potential as antioxidants, cancer therapeutic agents, and drug carriers [13]. Several investigations have found them to be anticancer, antioxidant, antibacterial, and anti-biofilm [14]. The use of nano-Se medicine in the treatment of Huntington's disease has yielded encouraging results. SeNPs are employed in photocells, photocopying, photometers, and xerography due to their unusual semiconducting, photoelectric, and X-ray sensing capabilities [15, 16].

2.3. Synthesis Methods of Selenium Nanoparticles

SeNPs have been synthesized using a variety of methods. These approaches are roughly classified into two types: biological and chemical reduction. Biological reduction approaches involve the conversion of various organic/inorganic selenium compounds to non-toxic and useful SeNPs using biological agents such as bacteria or plant extracts.

2.4. Chemical Reduction Method

Chemical reduction employs chemical compounds that reduce the element, its salt, or compounds, with the size controlled by surfactants or growth terminating reagents such as polyvinylchloride (PVP), folic acid, and others. Developed a stable colloidal solution of SeNPs for a variety of applications [17]. Synthesised spherical SeNPs about 13 nm in size using SeO2 as the precursor and PVP as the stabilising agent and potassium borohydride [KBH4] as the reducing agent in ice-cold solution [18]. The appearance of orange colour indicates due to formation of α-Se. According to transmission electron microscopy (TEM) investigation, the particle shape and size were 10 nm in diameter. Reported the usage of protein molecules to stabilise hollow SeNPs produced by mercaptoethanol reduction of sodium selenite [19]. The reaction was carried out at a low temperature (10 °C) and lasted nearly three days. The particles had an average diameter of about 30 nm and a shell thickness of 4 nm.

According to using ascorbic acid decreased sodium selenite using polyvinyl alcohol (PVA) as a stabilising agent, resulting in an average particle size of 70 nm as measured by dynamic light scattering (DLS) [20]. The absorption was measured between 250 and 450 nm. The use of hyperbranched polysaccharide as a stabiliser in the reaction of selenious acid with ascorbic acid in water resulted in the creation of very stable (>1 month) SeNPs with an average size of about 24 nm [21]. Because selenous acid a strong oxidising agent, it is easily reduced by SO2. The stabiliser was sodium dodecyl sulphate (SDS), and the reaction temperature was controlled at 80 °C. TEM was used to investigate the variation in particle size over time. In a time, span of 30 seconds to 4 minutes, the particle size ranged from 30 nm to 200 nm. Highlighted the usage of sodium thiosulfate as a reducing agent in their article [22]. Investigated the effect of SeNP size on methicillin-sensitive and methicillin-resistant Staphylococcus aureus (MSSA and MRSA) inhibition [23]. The SeNPs synthesised utilising the chemical reduction approach using polysaccharides as stabilizing/reducing agents were evaluated critically [24].

The microwave approach is now one of the most common chemical procedures for material production. The approach is quick, simple, economical, and clean, yields a high yield of the end product, and is frequently referred to as a green synthesis route. Microwave heating is more efficient than conduction heating because heating using microwave radiation is more uniform because the radiation interacts directly with the molecules. These benefits prompted researchers to use this approach for the production of SeNPs as well. However, the literature on the use of microwave energy (for the synthesis of SeNPs) is extremely limited. It was previously reported that the synthesis of both red and black SeNPs from cyclooocteno-1,2,3-selenadiazole is mediated by microwave radiation breakdown [25].

2.5. Hydrothermal Method

Shin et al. Reported the first usage of cellulose nanocrystals in the reduction of Na2SeO3 to create SeNPs with sizes ranging from 10 to 20 nm [26]. The process is both convenient and environmentally favourable. Another example of environmentally friendly synthesis is the work of Abbasian et al., who used coffee bean extract to decrease Na2SeO3 to See [27]. The reaction took 15 minutes to complete at a medium temperature. By reducing Na2SeO3 with hydrazine chloride, spherical nanoparticles with an average size of 15 nm were created.

2.6. Bioinspired Synthesis of Selenium Nanoparticle Using Bacteria

Physical and chemical methods of synthesis of nanoparticles confront obstacles and constraints that a biological approach could overcome [28]. The synthesis of SeNPs using this method has been shown to be safe, affordable, and environmentally benign, with no requirement for harmful components [29]. Various microorganisms, such as bacteria, algae, yeast, and fungi, are employed in the bioproduction of metalloid nanoparticles [30]. Under anaerobic or aerobic conditions, many bacteria might biosynthesize SeNPs via the detoxification process [31]. By using a cellular detoxifying mechanism that preserves redox potential as part of its respiratory chain of electron transfer, these bacteria could decrease selenite and selenate oxyanions, either as non-toxic Se0 or methylated Se species. Microorganisms biosynthesize SeNPs, but Se oxyanions are decreased and can accumulate in many forms, including intracellular, extracellular, and membrane-bound. The general mechanism of SeNPs synthesis is separated into two steps: (i) formation of Se0, which is accomplished by reducing selenate to selenite and subsequently reducing selenite to insoluble Se0, and (ii) formation of SeNPs, which comprises assembly and exporting out of the cell [32].

2.7. Mechanisms

The mechanism involved in intracellular synthesis of SeNPs involved two reductases, nitrite reductase and thiol-mediated reductase, work together to reduce selenite in Stenotrophomonas sp. EGS12 [33]. When selenite is reduced to Se0 in the cytoplasm, the production of Se0 atoms and, later, the assembly of Se nanospheres occurs. To avoid Se nanosphere build-up and accompanying necrosis, the cell must have an export mechanism for transporting Se nanospheres generated intracellularly [34]. T. selenatis forms Se nanospheres in the cytoplasm, which are then transported out of the cell. The procedure involves reducing selenite to Se0, which is then coupled to a SefA protein to form a Se nanosphere.

Selenium extracellular formation. When selenite is converted to Se0 in the cytoplasm, it is transported (as a foreign entity) across the cell membrane by an unknown export mechanism. Then, outside the cell, Se0 nuclei are assembled into Se spheres via an Ostwald-type mechanism that aids in ripening, as described for some bacteria in recent years, including Azospirillum brasilense, Stenotrophomonas maltophilia SeITE02, Burkholderia fungorum DBT1, Burkholderia fungorum 95, and Bacillus mycoides SelTE01 [35-37]. Demonstrated for the first time that Alcaligenes faecalis Se03 isolates from the intestine of Monochamus alternatus were capable of converting 1 mM and 5 mM sodium selenite concentrations into red amorphous Se0, primarily extracellular [38]. They discuss thioredoxin reductase, which is found in the cytoplasm of bacteria and is responsible for reduction by taking electrons from NADPH. In another work, Enterobacter cloacae Z0206 synthesised Se-NPs both intra- and extracellularly via the fumarate reductase enzyme using selenite reducing factor [39]. Due to their high surface energy, SeNPs synthesis could imply an Ostwald maturation mechanism in which small particles merge to make larger ones [32]. Other scientists hypothesize that molecules found on the SeNP surface, such as proteins, polysaccharides, or extracellular polymeric substances (EPS), operate as a cover or capping agent in the produced nanoparticle at the final stage of creation.

Oxyanion detoxification, microbial respiration with selenate/selenite as the ultimate electron acceptor, and several enzymatic processes are examples of reduction reactions. It is even claimed that thioredoxin reductase, nitrite reductase, or other membrane reductases, as well as thiol group molecules such as Glutathione and Bacilithiol, are involved in SeNPs formation in bacterial system [40, 41]. Extracellularly synthesised Bio-SeNPs from Lactobacillus acidophilus was found to suppress biofilm formation in drug-resistant bacte-

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ria S. aureus and E. coli [31]. Intracellular synthesis of SeNPs by halophilic strains uses cellular debris or dead inoculated bacteria [42]. Lactobacillus strains play a pivotal role in synthesis of selenium nanoparticles (SeNPs). Various parameters were standardized. As observed in various publications, the biotransformation to Se0 state requires sodium selenite as precursor substrate with various concentration as mentioned in Table 1. The UV vis spectroscopy shows surface plasmon resonance 385-400nm.

Table 1: Optimization Parameters of the Synthesis of SeNPs Mediated by Various Strains of Lactobacillus SP.

Strains used	pH	Temperature	Conc. Na_2SeO_3	Shape	Size	Colour	Ref
Lactobacillus paracasei HM1	6	20°C-35°C	4mM	Hexagonal	3-50nm	Dark red	(55)
Lactobacillus casei ATCC 393	5-6	37°C	20μg/mL	Spherical	300-450	Red	(54)
Lactobacillus pentosus ADET MW861694	4.5	37°C	4mM	Spherical	106.1 nm	Red	(53)
Lactobacillus brevis	4.5	30 °C	5 mM	Spherical	20-200nm	Pink, Red	(52)
Lactobacillus acidophilus	7.0	37 °C	15 mM	Spherical	2–15 nm	Red	(31)

2.8. Green Synthesis Using Plants

Plant-based synthesis of SeNPs has advantages over regular or standard synthesis procedures. The plant-based synthesis of SeNPs is an environmentally benign and cost-effective technique that employs natural stabilising and reducing agents. Plant extract-mediated nanomaterial synthesis began in the early twentieth century, and various plant species have been studied for their ability to decrease and stabilise SeNPs using Aloe vera leaf extract. It has been established that Aloe vera leaf extract contains several natural reductants and stabilisers such as sterols, polysaccharides, vitamins, phenolic compounds, organic acids, enzymes, lignin, flavonoids, and proteins that are secondary metabolites of plants that serve in the reduction [43].

The use of Vitis vinifera extract as a reducing and stabilising agent in the green synthesis of SeNPs. For example, in the presence of garlic clove extract (Allium sativum), Sharma et al., Described the green synthesis of SeNPs of varied sizes and forms [44]. Many other studies have been described to investigate the biosynthesis of SeNPs using Dillenia indica leaf extracts [45]. Spermacoce hispida aqueous leaf extract, Zingiber officinale fruit extract, Carica papaya latex, Citrus lemon fresh fruit extract, Roselle plant extract, Cinnamomum zeylanicum bark extract, and Prunus amygdalus leaves extract [45, 46].

2.9. Green Synthesis Using Fungi

The fungus Alternaria alternata was the first to be studied for mycosynthesis of SeNPs. Inoculum treated with sodium selenite produced nanoparticles ranging in size from 30 to 150 nm [47]. Aspergillus terreus was the fungus species reported for the extracellular selenium nanoparticles using SeO2 as a precursor within one hour. UV-visible spectroscopy, DLS, and EDX were used to characterize nanoparticles with diameters of roughly 47 nm [48]. Trichoderma sp., the most common plant symbiotic fungus, in combination with SeNPs synthesised from their culture filtrate, has effectively controlled Downy Mildew conditions in pearl millet fields. The nanoparticles ranged in size from 49.5 to 312.5 nm and demonstrated size-dependent activity against Sclerospora graminicola zoospores on chilly and tomato leaves [49]. The solid-state fermentation approach with Monascus purpureus ATCC16436 produced SeNPs with a diameter of 46.58 nm [50]. Yeast sp., like filamentous fungi, has demonstrated extraordinary characteristics in converting Se oxyanions to SeNPs. Magnusiomyces ingens LH-F1 was able to utilise SeO2 and synthesise SeNPs with sizes ranging from 70 to 90 nm. Two protein bands discovered on the surface of the nanoparticles by SDS-PAGE could be the explanation for particle stability. These SeNPs were found to have antibacterial action against Arthrobacter sp-W [51].

3. Conclusion

The importance of biogenic synthesis of SeNPs and green synthesis routes for biocompatibility and safety, it is expected that green synthesis of SeNPs will emerge as a major therapeutic tool with the potential to treat deadly cancers and a wide range of other devastating disorders such as neurodegenerative diseases, diabetes, viral infections, antimicrobial drug resistance, antifungal drugs, and environmental applications.

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