

A Review on Algal Mediated Synthesized Metallic Nanoparticles: An Eco-friendly Approach for Sustainable Nanotechnology

Abstract

The field of nanotechnology has witnessed a paradigm shift in recent years, with an increasing emphasis on eco-friendly and sustainable synthesis methods for metallic nanoparticles. Algal-mediated synthesis, an emerging and promising technique, harnesses the bioactive compounds present in algae for the green synthesis of metallic nanoparticles. This process not only offers a sustainable alternative to conventional chemical methods but also holds the potential to revolutionize various industries, including medicine, energy, and environmental remediation. Microalgae, forming a substantial part of the planet's biodiversity, are usually single-celled colony-forming or filamentous photosynthetic microorganisms, including several legal divisions like Chlorophyta, Charophyta, and Bacillariophyta. Whole cells of *Plectonema boryanum* (filamentous cyanobacteria) proved efficient in promoting the production of Au, Ag, and Pt nanoparticles. The cyanobacterial strains of *Anabaena flos-aquae* and *Calothrix pulvinata* were used to implement the biosynthesis of Au, Ag, and Pt nanoparticles. This abstract provides an overview of the key aspects of algal-mediated metallic nanoparticle synthesis. Algae, as a versatile source of bioactive compounds, serve as both reducing and stabilizing agents in the nanoparticle formation process. Various types of algae, including microalgae and macroalgae, have been explored for this purpose, each with distinct biochemical profiles that contribute to the synthesis process.

Keywords: Nanotechnology, Metallic Nanoparticles, Algae, Applications

Introduction

The synthesis of metal nanoparticles has attracted considerable attention in recent years due to their unique physicochemical properties and a wide array of potential applications. Traditional chemical methods for nanoparticle synthesis often involve the use of toxic chemicals and energy-

intensive processes, raising environmental concerns. In response to these challenges, the emerging field of green nanotechnology has paved the way for innovative and sustainable approaches to nanoparticle fabrication. Algae-mediated synthesis of metal nanoparticles has emerged as a promising and eco-friendly technique, harnessing the extraordinary capabilities of algae to reduce and stabilize metal ions, ultimately leading to the formation of nanoparticles.

Algae, a diverse group of photosynthetic microorganisms that encompass both microalgae and macro-algae (seaweed), have been widely explored for their ability to synthesize metal nanoparticles. This eco-friendly approach capitalizes on the unique biochemical composition of algae, which includes various secondary metabolites, such as polysaccharides, polyphenols, proteins, and enzymes, that play pivotal roles in reducing and capping metal ions during the synthesis process.

The mechanisms involved in algae-mediated metal nanoparticle synthesis are multifaceted. Typically, the process involves the following steps:

- 1. Biochemical Reduction:** Algae possess a range of bioactive compounds that can act as reducing agents. These compounds, often referred to as "bioreductants," are released by algae into the surrounding solution. When metal ions are introduced into this solution, these bioactive compounds initiate a redox reaction, reducing the metal ions to form metal nanoparticles. The specific compounds involved can vary depending on the type of algae used.
- 2. Stabilization:** In addition to their reducing capabilities, the bioactive compounds in algae also function as stabilizing agents. They interact with the newly formed metal nanoparticles, preventing them from agglomerating and maintaining their colloidal stability. The interaction between these compounds and nanoparticles may involve electrostatic forces, steric hindrance, or chemical bonding, depending on the nature of the bioactive compounds.
- 3. Shape and Size Control:** The inherent composition and structure of algae can influence the size and shape of the synthesized metal nanoparticles. Different species of algae possess unique combinations of bioactive compounds, leading to variations in the morphology and size

of the resulting nanoparticles. This tunability is advantageous for tailoring nanoparticles for specific applications.

4. Biocompatibility: One of the key advantages of algae-mediated synthesis is the biocompatibility of the resulting nanoparticles. Since the bioactive compounds in algae are biocompatible, the nanoparticles are often well-suited for biomedical applications, such as drug delivery, imaging, and therapy.

5. Environmental Sustainability: Algae-mediated synthesis is in alignment with the principles of green chemistry, as it minimizes the use of hazardous chemicals and operates at mild reaction conditions. This eco-friendly approach is characterized by its reduced environmental footprint, making it an attractive choice for sustainable nanotechnology.

“Among various microorganisms, microalgae are primitive microscopic plants, and they have significant advantages as cell factories for the production of nanoparticles compared to larger plants. Algae are aquatic filamentous photosynthetic organisms that fall under the kingdom of plantae. All these algae are broadly classified into two types: microalgae and macro algae” (Leaf et al., 2020). “Macro algae can be counted under the naked eye whereas microscopes are required to observe microalgae. Unlike most biomass, both the algae can be harvested several times in a single year. Algae also have the ability to grow without the help of any addition of outside chemicals or fertilizers. Microalgae grow extremely quickly and, on average, double their mass 10fold faster than higher plants. It is known that various species of microalgae reduce metal ions”. (Jacob et al., 2021)

“Algae are recognized as primitive microscopic plants and have few advantages, such as growth rate and nutrient requirements, for producing nanoparticles compared to higher plants” (Jacob et al., 2021). The present review makes an attempt to improve researchers’ knowledge of green synthesis methodology of nanoparticle synthesis using different algal species and their various pros and cons.

Classification of Nanomaterials and Methods of Synthesis

Nanomaterials are materials with at least one dimension on the nano scale, typically ranging from 1 to 100 nanometers. They exhibit unique properties and behaviors compared to bulk materials, making them highly valuable for various applications, including electronics, medicine,

energy, and more. Nanomaterials can be classified based on their composition, structure, and properties and they can be synthesized using various methods. Here's an overview of the classification of Nanomaterials and common synthesis methods:

a. Organic Nanoparticles

“Organic nanoparticles are composed of either natural or synthetic carbon-based molecules or come in various categories, such as micelles, protein/peptides, liposomes, dendrimer-based nanoparticles, capsules, polymer conjugates, polymersomes, and polymeric NPs. Their properties, such as size, shape, and content, are greatly affected by these factors. While organic nanoparticles are generally safe, biocompatible, and biodegradable, they can be prone to degradation at high temperatures due to intracellular enzymes present in cells. Examples of organic NPs include Poly-L-lysine, quaternary ammonium compounds, cationic quaternary polyelectrolytes, N-halamine compounds, and algae and chitosan. Because of their instability at high temperatures, organic NPs are often preferred for their antibacterial properties” (Jain et al., 2014).

b. Inorganic Nanoparticles

“Inorganic nanoparticles are materials with nanometer-scale dimensions composed of non-carbon elements, including metals, metal oxides, and nonmetals. These nanomaterials possess unique physicochemical properties such as high surface area, high reactivity, and tunable–optical properties that make them suitable for a broad range of applications in various fields such as biomedicine, electronics, energy, and environmental remediation” (Pareek et al., 2017, Shnoudeh et al., 2019).

c. Metal Nanoparticles

“Metallic nanoparticles (M-NPs) are inorganic nanoparticles that have a metal or metal oxide core that is typically covered by an organic or inorganic material or metal oxide shell. M-NPs have numerous properties, such as mechanical hardness, large surface area, low melting point, and optical and magnetic characteristics. Metallic-nanoparticle-based catalysts are highly active and selective and have a long life for various chemical processes. Commonly studied M-NPs include silver, gold, copper, titanium, platinum, magnesium, and zinc NPs. Nanomaterials can be categorized based on the number of dimensions they possess at the nanoscale, including zero, one, two, and three dimensions. Nanoparticles, which have all dimensions less than 100 nm, belong to the zero-dimensional-nanomaterial category. Metal nanoparticles have received considerable attention from the scientific community worldwide owing to their distinctive surface-plasmon resonance and optical properties” (Seabra, 2015).

d. Metal Oxide Nanoparticles

“The reaction between a metal cation and oxygen gas results in the formation of metal oxides. Metal oxides (MOs) are an interesting class of inorganic compounds that have attracted much research and study due to their wide range of properties and characteristics. The useful magnetic, electrical, and optical properties of transition metal oxide nanoparticles make them a significant class of materials” (Zeng et al., 2022, Meng et al., 2022). “This makes them more suitable for a range of uses, including sensors, catalysis, batteries, lithium-ion, and environmental applications, among others. Transition metal oxides have a variety of fascinating properties that make them deserving of study in various applications when compared to other classes of materials” (Seabra, 2015). “The nature of metal oxides is more complex than that of pure metals, and their bonding can range from being almost ionic to being extremely covalent or even metallic. There are many different types of metal oxides, and each has its composition, morphology, structure, and physicochemical properties. Metal oxide nanoparticles, in particular, are of interest due to their significant and amazing optical, electrical, and magnetic properties” (Srivastava et al., 2013). Metal oxide nanoparticles (MONPs) are highly useful in a wide range of industrial activities, including sensors, electronics, solar energy conversion, catalytic processes, and magnetic-storage media.

e. Non-metallic Nanoparticles

“Non-metallic nanoparticles are generated using non-metallic elements, which consist of various non-metal elements from distinct groups in the periodic table, including group IV elements (such as carbon and silicon) and group V elements (such as phosphorus). Doped nanoparticles, on the other hand, are often produced by incorporating Group V elements with other metals and nonmetals. Phosphate and phosphorus combine to generate ceramic nanoparticles. Nonmetal nanoparticles, for example, graphene, fullerenes, carbon nanotubes, and silica, have a distinctive structure and a large surface area, are biocompatible, have intriguing redox and catalytic capabilities, and are mechanically stable” (Fawcett et al., 2017).

“Nanoparticles are characterized by their synthesis process. For the synthesis of nanoparticles, there are several methods available. Synthesis by using physical and chemical methods is quite costly and produces toxic by-products. For nanoparticle synthesis, two approaches exist: bottom-up and top-down” (Shukla et al., 2021). “The first step is the attrition of large macroscopic particles. The most common technique employing the role of the top-down approach for nanomaterial synthesis is the lithographic interferometric” (Agarwal et al., 2017). This technique involves the synthesis by self-assembly of nanoparticles of miniaturized atomic components. It is a relatively inexpensive approach. It is based on the approach to the kinetic and thermodynamic balance.

Phyconanotechnology by different species of microalgae

Phyconanotechnology, also known as microalgal nanotechnology, is an emerging field that focuses on harnessing the unique properties of microalgae to develop nanomaterials and applications. Different species of microalgae are being explored for their potential in this field. Here are some key aspects of phyconanotechnology by different species of microalgae:

Various microalgae species are being studied for their ability to produce nanomaterials or serve as a source of raw materials in nanotechnology applications. Selection depends on the specific properties of the microalgae, including their growth rate, lipid content, and the ability to synthesize or secrete nanomaterials. Some microalgae have been found to naturally synthesize

and secrete nanoparticles. For example, some diatom species can produce intricate silica nanoparticles with well-defined shapes. Researchers have been able to modify growth conditions to control the size and shape of these nanoparticles, making them valuable for various applications. Microalgae can serve as biogenic factories for the synthesis of nanomaterials. They can accumulate and store metal ions from the environment, which can then be used to synthesize metal nanoparticles. This process, known as biomineralization, is being studied for applications in catalysis, sensing, and environmental remediation. Microalgae produce extracellular polymeric substances (EPS), which play a role in biofilm formation. These EPS can be used in nanotechnology to modify the properties of surfaces, create biosensors, and enhance drug delivery systems. Microalgae are being explored for their ability to remove heavy metals and other pollutants from water. The absorbed or adsorbed nanoparticles can be recovered and used in various applications, including in the synthesis of new nanomaterials. Phyconanotechnology by different microalgae species has a wide range of potential applications. These include drug delivery, tissue engineering, wastewater treatment, biosensing, and the production of biofuels. Microalgal nanoparticles and biopolymers have properties that make them suitable for these applications. Phyconanotechnology is often considered more sustainable and environmentally friendly compared to traditional methods of nanomaterial synthesis, which often involve harsh chemicals. The use of microalgae can reduce the environmental footprint of nanotechnology processes. While microalgae show promise in phyconanotechnology, there are challenges, such as optimizing growth conditions, scaling up production, and ensuring consistent nanoparticle quality. Additionally, research is ongoing to understand the mechanisms of nanoparticle synthesis by microalgae fully.

Mechanism of algae mediated biosynthesis of nanoparticles

The mechanism of algae-mediated biosynthesis of nanoparticles involves a series of biological and chemical processes. Algae, as microorganisms with unique biochemical properties, can reduce metal ions and stabilize the resulting nanoparticles. The understanding and selection of biocatalysts, the application of optimum conditions for cell growth and enzyme activity and the utilization of suitable mediated organisms are significant for the production of high-quality nanoparticles. The existence of the constituents is very important as the biological component

and biomolecules are believed to be responsible for the reduction of metallic ions into nanoparticles.

Algae-Assisted Synthesis

Algae-assisted synthesis refers to a process where algae, typically microalgae or macro algae, play a significant role in assisting or facilitating the synthesis of various materials, including nanoparticles, biofuels, and organic compounds. This approach leverages the unique biological and chemical properties of algae for sustainable and eco-friendly production.

Nanoparticles synthesis: Algae can be used as reducing and stabilizing agents in the synthesis of nanoparticles, such as silver, gold, and iron nanoparticles. Algae-mediated nanoparticle synthesis is an environmentally friendly alternative to conventional chemical methods and is employed in various applications, including nano medicine and environmental remediation.

Biomineralization: Some algae can naturally secrete or precipitate minerals, such as calcium carbonate or silica, which can be used as building materials or for the synthesis of advanced materials. Diatoms, a type of microalgae, are known for their ability to produce

Bioremediation: Algae are employed in bioremediation to clean polluted environments. They can take up and accumulate heavy metals, organic contaminants, and other pollutants from water and soil. These contaminants can be harvested and utilized for various purposes.

Biofuel production: Algae are a promising source of biofuels, such as biodiesel and bioethanol. They can convert sunlight and carbon dioxide into lipids or carbohydrates that can be converted into biofuels. Algae-assisted synthesis involves optimizing the growth conditions to maximize biofuel production.

Phycoremediation: Algae can remove excess nutrients, such as nitrogen and phosphorus, from wastewater, thus helping to clean polluted water bodies and providing a sustainable approach to managing nutrient pollution.

Nutrient recycling: Algae can be used to recycle nutrients in aquaculture systems by converting waste from fish farming into algae biomass, which can be used as feed or bio fertilizer.

Sustainable Materials: Algae can be used in the development of sustainable materials, such as biodegradable plastics and bio composites, reducing the reliance on fossil-based materials.

Synthesis of different NPs Using Algae

1. Biosynthesis of AgNPs

“Algae are a suitable and worthwhile source for the production of metallic nanoparticles given their abundance and simplicity of access” (Govindaraju et al., 2008). “The synthesis of nanoparticles using algae can be accomplished in three steps: (a) preparation of algal extract in water or an organic solvent by heating or boiling it for a set period, (b) preparation of molar solutions of ionic metallic compounds, and (c) incubation of algal solutions and molar solutions of ionic metallic compounds under controlled conditions, either with continuous stirring or without stirring” (Jasni et al., 2021). NP production is dose-dependent and also depends on the kind of algae (Benelli, 2019) employed. “Metal reduction is caused by a range of biomolecules, including polysaccharides, peptides, and pigments. Proteins, via amino groups or cysteine residues, and sulfated polysaccharides, stabilize and cap metal nanoparticles in aqueous solutions” (Shrivastava et al., 2016). The synthesis of nanoparticles using algae requires less time than the other biosynthesizing processes. Several seaweeds, including *Sargassum wightii* and *Fucus vesiculosus*, have been utilized to create silver nanoparticles (Ali et al., 2011, Annadhasan et al., 2014, Apte et al., 2013, Buzea et al., 2007, Chen et al., 2013, Chugh et al., 2021, Ebrahimezhad et al., 2016, El-Kassas and Ghobrial, 2017, Ghodake et al., 2018) of various sizes and forms.

2. Biosynthesis of Zinc Oxide NPs

“Algae are classified based on their cell walls’ chemistry, the presence of flagella, and other characteristics, with microalgae and macroalgae falling into different categories. However, the most widely used classification feature for algae is the presence of specific pigments other than chlorophyll. This helps in identifying macroalgae, which can be classified as green algae (Chlorophyta), brown algae (Phaeophyta), and red algae (Rhodophyta), the three primary

classified types of algae. Microalgae, which are the most primitive and simply organized members of the plant kingdom, typically exist as cells measuring about 3–20 μm . They are found widely and are ubiquitous, with aquatic microalgae being discovered in various locations, such as hot springs and glacial ice flows. Several chemical components that can be extracted from macro- and microalgae include polysaccharides, vitamins, lipids, proteins, dietary fiber, antioxidants, minerals, and polyunsaturated fatty acids” (Abbas et al., 2019). “To give a brief example, among the potential chemical compounds effective in cancer treatments are some phytochemicals like carotenoids, pigment, scytonemin, several calothrixins, and phlorotannins” (Almeida et al., 2020).

3. Biosynthesis of Copper Oxide NPs

“The environmentally accepted ‘green chemistry’ idea has been applied to the biosynthesis of nanoparticles for the creation of clean and environmentally friendly nanoparticles, which incorporates bacteria, fungi, plants, actinomycetes, and other organisms, and is referred to as ‘green synthesis’. Biosynthesis of nanoparticles utilizing the organisms mentioned above exemplifies a green alternative for the creation of nanoparticles with novel characteristics. Unicellular and multicellular organisms are permitted to respond in these syntheses. Plants are renowned as nature’ chemical factories since they are low-cost and low maintenance. Because extremely minute quantities of these heavy metals are hazardous even at very low concentrations, plants have shown exceptional potential in heavy metal detoxification as well as accumulation, through which environmental contaminants may be overcome” (Sutradhar et al., 2014, Aminuzzaman et al., 2017). Nanoparticle synthesis using plant extract has benefits over other biological synthesis methods, such as microorganisms, because the rate of metal nanoparticle synthesis with the help of plant extract is more persistent (Aminuzzaman et al., 2016), significantly faster (Makarov et al., 2014, Ahmed et al., 2016), and extremely mono-dispersive (Sarkar et al., 2020) in respect to their biological methods.

“The main challenges for using microorganisms include the toxicity of certain bacteria, the isolation procedure of microorganisms, and the tedious incubation procedure which make the suitable for many researchers. Plant extracts are therefore are markable source of synthesis of

metal and metal oxide nanoparticles. Additionally, the reaction kinetics of plant-assisted nanoparticle synthesis is much faster than other biosynthetic methods that are comparable to chemical nanoparticle production. Plant components such as fruit, leaf, stem, and root have been frequently employed for the green route of nanoparticle production due to the high-quality phyto-chemicals they generate. Here, for the mentioned reason, Copper oxide nanoparticles have been widely synthesized using various plant extracts” (Ghidan et al., 2016). “In this plant-based manufacturing process, the metal salt is mixed with the plant extracts, and there action takes 1-3h to complete at room temperature. Plant extracts include a variety of bioactive metabolites, including flavonoids, phenols, proteins, terpenoids, and tannins, which serve as reducing and stabilizing agents, transforming metallic ions in to nanoparticles” (Asemani and Anarjan 2019). The plant extract produces electrons, which cause copper salts to get reduced. Copper oxide nanoparticles are formed when phyto chemicals react with copper ions, resulting in reduction.

Application of Algae-Mediated Nanomaterials

“Algae belonging to Cyanophyceae, Chlorophyceae, Phaeophyceae, and Rhodophyceae families have been used as nano-machines by intracellular and extracellular synthesis of gold (Au), silver (Ag), and other metallic nanoparticles. Algae are an attractive medium for the processing of diverse nanomaterials, owing to the inclusion of bioactive compounds in their cell extracts such as pigments and antioxidants that serve as biocompatible reductants. Silver nanoparticles synthesized in an environmentally friendly manner effectively inhibit bacterial growth by eliciting bactericidal activity against Gram-negative and Gram-positive biofilm-forming pathogens. As a result, silver nanoparticles produced by *G. amansii* (brown algae) may serve as potential anti-fouling coatings for a variety of biomedical and environmental applications” (Pugazhendhi et al., 2018; Yulia A. Yugay et al., 2023). Nanoparticles produced by algae can compete with standard drugs and have been shown to have antibacterial, anticancer, and antifungal effects. Aside from medical uses, metal nanoparticles have a broad variety of applications in computing, optics, cosmetics, and other areas.

Antioxidant Activity

Defatted algal biomass was reported for synthesis of silver nanomaterial by (Chokshi et al., 2016). “After lipid extraction, the residual biomass of the microalgae *Acutodesmus dimorphus*

was used by the researcher to make a micro-algal water extract, which was then used to make silver nanoparticles (with a scale of 2–20 nm). The antioxidant ability of the biosynthesized silver nanoparticles was assessed using 2,2'-azino-bisphosphate (3-ethylbenzothiazoline-6-sulfonic acid)" (Chokshi et al., 2016).

Antibacterial Activity

“Antibacterial behavior of nanoparticles synthesized from algae has been studied against a variety of bacterial strains. Silver nanomaterials manufactured from the brown seaweed *Padina tetrastromatica* effectively slowed the growth of *P. aeruginosa*, *Klebsiella planticola*, and *Bacillus subtilis*” (Sangeetha et al., 2012). “Another research found that robust and colloidal-shaped silver nanomaterials made from an aqueous extract of the green marine algae *Caulerpa serrulata* had excellent anti-microbial activity against *Shigella* sp., *S. aureus*, *E. coli*, *P. aeruginosa*, and *Salmonella typhi* at lower concentrations. *E. coli* had the largest zone of inhibition of 21 mm, while *S. typhi* had the smallest zone of inhibition of 10 mm at 50µl solution of silver nanomaterials” (Aboelfetoh et al., 2017; Saleh AlNadhari et al., 2021).

Antifungal Activity

The antifungal function of nanoparticles is defined by their size and form. The broad surface region of small nanoparticles ensures that microbial growth is inhibited. The enhanced contact area of the spherical form with size-reduced ions eliminates growth of fungus.

Conclusion:

Algal Mediated Synthesized Metallic Nanoparticles: An Eco-friendly Approach for Sustainable Nanotechnology" explores a green and sustainable method for producing metallic nanoparticles using various species of algae. This eco-friendly approach leverages the unique properties of algae to reduce and stabilize metal ions, resulting in the formation of nanoparticles. The article highlights the potential applications of these algae-mediated nanoparticles in fields such as Nano medicine, catalysis, and environmental remediation. Additionally, it emphasizes the environmental and economic advantages of this approach, as it reduces the need for harsh chemical reagents and processes. This innovative technique offers a promising and biocompatible solution for the sustainable development of nanotechnology. The concept of

'green chemistry' is specified to reduce the generation of wastes and by-products, decrease the usage of hazardous chemical substances and energy demands by incorporation of renewable and natural resources. The application of biotechnology and the allied fields are seen as an important scientific discipline for the major contribution toward the achievement of sustainability

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