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METALLIC NANOPARTICLE SYNTHESIS FROM MICROALGAL EXTRACTS VIA GREEN TECHNOLOGY

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Abstract

This method is gaining popularity due to its simplicity, cost-effectiveness, and eco-friendliness. The microalgae extract contains various bioactive compounds that not only reduce the metal ions but also stabilize the nanoparticles. The size, shape, and morphology of the nanoparticles can be controlled by varying the experimental parameters such as the concentration of the microalgae extract and the metal ion solution, pH, and temperature. The synthesized nanoparticles can be used in various applications such as catalysis, biomedicine, and environmental remediation. This review focuses on the recent advancements in the green synthesis of metal nanoparticles using microalgae extract, the various experimental parameters involved, and their applications.

One of the well-known metal oxide nanoparticles with considerable applicability in numerous sectors and research facilities are zinc oxide nanoparticles (ZnO NPs). To fulfill the increased demand for ZnO NPs, a variety of synthetic techniques have been used in their manufacturing. The search for additional options with environmental and economic advantages is a result of the economic and environmental disadvantages associated with the majority of ZnO NP production methods. Surprisingly, the biological approach of synthesis employing plant sources has been proven suitable for the manufacture of ZnO NPs due to its multiple medical, healths, environmental, and economic benefits. Despite the advantages of biosynthesized ZnO NPs that have been described, there are still mysteries surrounding the creation method and responses. This article summarized the most recent developments in the biosynthesized ZnO NP's synthesis, mechanism approaches, characterization techniques, and applications in the textile, medical, and agricultural industries.

Keywords- Zinc oxide nanoparticles (ZnO-NPs), XRD, Zone of Inhibition, Metal Oxide, etc.

1. Introduction

Marine algae are well-known as functional food for their richness in lipids, minerals and certain vitamins, and also several bioactive substances like polysaccharides, proteins and polyphones, with potential medicinal uses against cancer, oxidative stress, inflammation, allergy,lipidemia, hypertensive and other degenerative diseases (Zuercher et al., 2006; Wada et al., 2011; Mohamed et al., 2012; Namvar et al., 2012). Thus, their phytochemicals include hydroxyl, carboxyl and amino functional groups, which can serve both as effective metal reducing agents and as capping agents to provide a robust coating on the metal NP in a single step (Mahdavi et al., 2013). Synthesis of cadmium sulphide NP using Phaeodactylum tricornutum was reported (Scarano and Morelli, 2003). Bio-reduction of gold by Rhizocloniumriparium, Navicula minima, and Nitzschia obtusa has been reported (Kalabegishvili et al., 2012). The bio-reduction mechanism involves the main phases such as activation, growth and termination. The activation phase includes reduction of metal adjacent NP into larger size particles accompanied by thermodynamic stability (Ostwald ripening); the termination phase comprises the final shape of NP (Mohamed et al., 2012).

Green syntheses are environmental friendly alternatives to conventional synthesis techniques. They aim to reduce toxic elements used or produced in conventional methods. Moreover, they benefit from sustainable sources and can reduce production cost, in practical and up-scalable manner (Tan et al., 2020). In this process, the microalgae extract acts as a reducing agent, which reduces the metal ions to form metal nanoparticles. The specific properties of ZnO NPs synthesized from plant extracts improved their use as fertilizers, insecticides, and fumigants in agriculture. ZnO NPs produced using photosynthetic processes have found notable success in the manufacture of compounds that are antimicrobial, antifungal, anticancer, antioxidant, anti-inflammatory, and anti-diabetic (Rizwan et al., 2018).

The synthesis depends on many parameters like temperature, pH, and substrate concentration, stirring and static conditions. It is hypothesized that the enzymes secreted by algal cells take parts in the bio-reduction of metal ions, followed by NP nucleation and growth. The intracellular synthesis depends on physico-chemical parameters like temperature, pH and concentration of the substrate (Han et al., 2019). The surface bound proteins and their residual

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amino acids viz cysteine, tyrosine and tryptophan play a vital role though –NH2 (amine) groups in NP capping and stabilization at basic pH. The extracellular and intracellular syntheses of GNP using the brown marine algae such as Sargassum muticum and Tetraselmisko chinensisare being reported by many researchers (Namvar et al., 2015; Azizi et al., 2013).

Zinc nanoparticles (ZnONPs) have been extensively studied for many decades due to their unique features and wide range of applications. Their uses include catalysis bio-sensing, imaging, and antibacterial activity. Antibacterial activities have gained much attention because they potentially offer a solution to the problem of antibiotic resistance (Prabu, 2018). ZnO NPs are increasingly used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical and chemical properties. These include optical, electrical, and thermal, high electrical conductivity, and biological properties. Due to their peculiar properties, they have been used for several applications, including as antibacterial agents, in industrial, household, and healthcare-related products, in consumer products, medical device coatings, optical sensors, and cosmetics, in the pharmaceutical industry, the food industry, in diagnostics, orthopedics, drug delivery, as anticancer agents, and have ultimately enhanced the tumor-killing effects of anticancer drugs (Jayanthi and Rao, 2016).

The physicochemical properties of nanoparticles are important for their behavior, bio-distribution, safety, and efficacy (Devarajan et al., 2018). Therefore, characterization of ZnO NPs is important in order to evaluate the functional aspects of the synthesized particles. Characterization is performed using a variety of analytical techniques, including UV-vis spectroscopy, X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Due to its environmentally friendly nature and a weed coupled with its reducing properties (Mabrouk et al., 2022).

Zone of inhibition in the plate showed that zinc nanoparticles synthesized using microalgae have the antibacterial activity against test pathogens namely Staphylococcus aureus, Listeria monocytogenes, Pseudomonas aeruginosa (Sathishkumar et al., 2019). Zone of inhibition was measured and compared with control of plant extract. On comparison with the synthesized ZnO nanoparticles and the plant extract outperformed in the bactericidal effect. Further, the zinc nanoparticles revealed to possess an effective antibacterial property against Bacillus cereus and Staphylococcus aureus. The present study emphasizes the use of plant medicinal for the synthesis of zinc nanoparticles with the potent antibacterial effect. Nanoparticles, including as metal oxide nanoparticles, carbon nanotubes, zerovalent nanoparticles, and nanocomposites, have a lot of potential for utilization in various wastewater ecosystems (Singh et al., 2019).

Metal oxide nanoparticles are mostly synthesized through physical and chemical procedures, however these techniques call for the employment of incredibly dangerous and reactive-reducing chemicals like sodium borohydride and hydrazine hydrate (Szczglewska et al., 2023). Major difficulties are also presented by using sophisticated apparatus, challenging procedures, and severe experimental settings. Chemical processes use artificial capping, reducing, and stabilizing chemicals to make the necessary homogenous metallic nanoparticles with less damaging consequences than physical approaches, which often yield heterogeneous nanoparticles and demand significant energy inputs. However, due to their possible impacts on people, physical and chemically created nanoparticles cannot be employed in medicine.

In recent years, there has been a lot of interest in the use of biological elements such microbes, extracts, and enzymes as reducing and stabilizing agents in the green synthesis of nanoparticles. The utilization of biological components for nanoparticles synthesis has a number of benefits over conventional chemical processes, including economic effectiveness, biocompatibility, and environmental friendliness (Salem and Fouda, 2021). In addition, using biological elements as reducing agents is a more affordable and environmentally friendly option than using conventional chemical synthesis techniques.

Microalgae are plants that are simple to cultivate all year long. Micro alga typically resides in the oceans and seamlessly blends into the geographical Indonesia. The higher plants do not include microalgae because they lack the traits and capabilities of such plants (Elkhatat and Al-Muhtaseb, 2023). Due to their photosynthetic activity, microalgae, also known as primary producers, are photosynthetic prokaryotic and eukaryotic microorganisms (Okada et al., 2020) that form the foundation or start of the aquatic food chain. Humans can profit from the chemicals produced by photosynthesis by using them as supplements (Koyande et al., 2019), biofuel (Galassco et al., 2019), and pharmaceuticals (Rodriguez-Concepcion et al., 2018).

2. Classification of Nanoparticles

Recent science has made nanotechnology a hot topic for researchers. With a size range of 1-100 nm in one dimension, nanoparticles are employed extensively in atomic physics, medical chemistry, and all other domains that are now known. There are several different types of nanostructured materials, including nanoparticles (NP) (Castro-Longoria et al., 2011), nano-pores (Philip, 2010), and nanotubes (Indira et al., 2013).

The NP is among all the core components of nanotechnology. Numerous domains, including physics, chemistry, electronics, optics, materials science, and the biomedical sciences, have extensive uses for the NP (Indira et al., 2012). There are numerous varieties of NPs, including gold (Indira et al., 2011; Srivastava et al., 2013), silver (Srivastava et al., 2013; Logeswari et al., 2015), zinc, titania (Ahmed et al., 2015; Ahmad et al., 2015), zirconium (Raliya et al., 2015;

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Indira et al., 2014a), strontium (Indira et al., 2014b), and others, that can be employed for various applications. Out of all of these, the literature has primarily discussed the gold and zinc NPs. Nanoparticles on the basis of their properties are of several types:-

1. Shape and Dimensions

- Zero Dimension- Quantum dots, coreshell, onion, hollow spheres
- 1D- Films, coatings, multilayer
- 2D- Tubes, fibres, wires, platelets
- 3D- Particles, Quantum dots, hollow spheres

2. Phase Composition

- Single Phase solids- Crystalline, amorphous particles and layers
- Multi Phase solids- Matrix composites, coated particles
- Multi-Phase Systems- Colloids, aerogels, ferrofluids

3. Nature of Material

- Pure Metals- Ag, Au, Cu, Fe, Ni, Co
- Metallic Oxides- ZnO, CuO, TiO₂, Fe₃O₄, CrO₂
- Metallic Chalcogenides- PbS, ZnS, CdS, ZnSe, CdTe, HgS, CuInSe
- Bimetallic- Ag-Au, Zn-Ag, Pt-Ni, Co-Mo
- Organic- CNT, Fullerene, Graphene Oxide

3. Biosynthesis of Nanoparticles by using biological agents

For NP synthesis, physical and chemical procedures are more common, but their use is restricted since they are expensive and use harmful materials (Salam et al., 2012). There are secure green eco-friendly methods accessible to solve these problems (Narayanan and Sathivel, 2011). The advantages of green synthesis over chemical and physical approaches include being more cost-effective, easier to scale up for large-scale NP syntheses, and not requiring the use of harmful chemicals or high temperatures or pressures. One of the more well-known areas of research in NP synthesis is phytonanotechnology (Davis et al., 2003). Algae are also employed as a "bio-factory" to create metallic nanoparticles. Seaweeds stand out among other types of bio-reductants because of their superior ability to absorb metals, low cost, and macroscopic structure (Asmathunisha and Kathiresan, 2013). Coral reefs include calcium that is arranged in important architectures, while diatoms and sponges are built with silica nanostructured covers. Biological organisms from marine resources are also typical nanostructures as shown in Figure 1. Several marine-derived organisms have been utilized to synthesize various NP, including lead, silicon-germanium, and cadmium, gold, and silver, zinc (Jena et al., 2014).

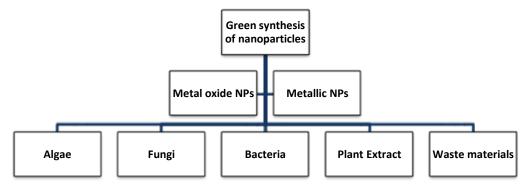


Figure 1: Several biological agents used for biosynthesis of Nanoparticles.

4. Nanoparticles synthesized by microalgae

Microalgae have a great capacity to absorb metal ions and, through a detoxifying process, create nanoparticles. Using the unicellular green microalga Scenedesmus sp., the study investigated the intracellular and extracellular biogenic synthesis of SNP (Shankar et al., 2016). Inside-the-cell nanoparticle high rates of AgI ion accumulation in the microalgal biomass and the consequent development of spherical crystalline SNP served as the catalyst for the start of biosynthesis. Additionally, the extracellular synthesis using boiling extract revealed the development of well-dispersed, extremely stable, spherical SNP with an average size of 5–10 nm. The creation and stabilization of SNP are mostly caused by biomolecules, proteins, and peptides, according to the FT-IR spectra (Verderio, 2014).

In addition, the synthetic NP demonstrated strong antibacterial action against dangerous gram-positive and gramnegative bacteria. A simple, affordable alternative template for the biosynthesis of nanomaterials in a large-scale system

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is provided by the use of such microalgal systems, which could be very helpful in biological applications (Grasso et al., 2019).

In order to evaluate the absorption, recovery, and generation of GNP, Lyngbyamajuscula, Spirulina subsalsa, and Rhizoclonium hieroglyphicum were subjected to radioactive and stable gold solutions (Chakraborty et al., 2006). The bio-reduction and stabilization of SNP were discovered to be aided by amines, peptide groups, and secondary metabolites flavonoids and terpenoids in an environmentally friendly synthesis of SNP employing the marine macroalgae Chaetomorphalinum (Kannan et al., 2013). In a conical flask with 100 L of 1 M zinc nitrate and 99.9 mL of seaweed extract, a quick synthesis of SNP was observed (Kumar et al., 2012). For the reduction of metal ions to take place where the phenolic compounds, amide I group, and aromatic rings implicated in the stabilisation of SNP, the extract was gradually heated to 60°C for 20 min in a heating mantle. The Candida albicans and Candida glabrata are effectively inhibited by the biosynthesized SNP from Gracilaria corticata. The protein released by Oscillatoria willei is in charge of the stabilisation of SNP and the reduction of zinc ions (Ali et al., 2011).

The reaction between zno ions and the Cystospore moniliformis extract produced SNP and resulted in a change in colour from greenish to pale yellow (Prasad et al., 2013). The spherical NP with monodispersity was clearly visible in the SEM pictures at reaction temperatures of 65°C and 75°C. Due to their small size, orientation, and physical characteristics, nanoparticles are widely employed because they have been demonstrated to alter the performance of any other substance that comes into touch with them. The UV-Vis Spectrophotometer, FTIR, DLS, Zeta Analysis, XRD, and SEM were used to characterize the nanoparticles. The discovered nanoparticles range in size from 160 to 180 nm (Verderio, 2014).

Additionally, it was discovered that the resultant ZnNPs were efficient against both gramme positive (Bacillus cereus, Staphylococcus aureus, Listeria monocytogenes) and gramme negative (Shigellaflexineri, Pseudomonas aeruginosa, Escherichia coli) bacteria. As a substitute strategy, the synthesis of silver nanoparticles from plant extract has become more popular. Silver nanoparticles were created using a plant extract (Sadia et al., 2023). After 72 hours of incubation at room temperature, the syntheses of NP utilizing the aqueous leaf extract of the brown seaweed Padina tetrastromatica. Sargassum cinereum seaweed extracts were utilized as a reducing agent in the environmentally friendly extracellular production of SNP from an aqueous solution of silver nitrate (Jegadeeswaran et al., 2012).

With a reaction temperature of 100°C, a seaweed extract concentration of 10%, and a residence time of 3 h, a high conversion of silver ions to SNP was accomplished. With 2.5 L (25 g/disc), the antimicrobial properties of NP were evaluated against the bacterium Staphylococcus aureus. Salmonella typhi, Proteus vulgaris, and Enterobacter aerogenes all showed significant growth inhibitions at values of 100 g/disc. The marine Cyanobacterium Phormidiumtenue NTDM05 was used in the manufacture and characterization of cadmium sulphide (CdS) nanoparticles (Mubarak Ali et al., 2012). Leptolyngbyav alderianum was discovered to be a successful bio-reagent for the creation of nano zinc. The brown biomass of Leptolyngbya sp. after 72 h of dark exposure in 9 mM AgNO3 solution served as an indicator of the nanozno formation at intracellular level. After being characterized, intracellular zinc particles from the zinc-loaded biomass were collected and tested for antibacterial qualities (Roychoudhury and Pal, 2014).

Nano-	Algal species	Size of NPs	Shape of NPs	Mode of
particles		(nm)		Synthesis
Zn	Brown & Cystophora	50–100	Spherical	Extracellular
	moniliformis			
	Chaetomorphalinum	03–44	Clusters	
	Cystophora moniliformis	50–100	Spherical	
	Enteromorpha compressa	40–50		
	Gracilaria corticata	18–46		
	Leptolyngbyav alderianum	02–20		Intracellular
	Oscillatoria willei	100-200		Extracellular
	Porphyra vietnamensis	13±03	Spherical	
	Sargassum cinereum	45–76	Triangle	
	Sargassum longifolium		Spherical	
	Spirogyra varians	35	Squasi-Spheres	Extracellular
	Ulva flexousa	02–32	Circular	
	Ulva lactuca	25–56	Spherical	
	Urospora sp.	20–30		Extracellular
	Spirogyra varians	35	Squasi-Spheres	Extracellular
	Ulva flexousa	02–32	Circular	
Au	Brown & Eckloniacava	30 ± 0.25	Spherical &	
			Triangular	
	Brown & Fucusvesiculosus	Varied	Spherical	

Table 1: Algae mediated synthesis of metallic Nanoparticles.

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	Chlorella vulgaris	02-10	Spatial array	
	Lyngbyam ajuscula	02–25	Spherical &	Intracellular
			Hexagonal	
	Padina gymnospora	53–67	Spherical	Extracellular
Cds	Phormidium tenue	05		Extracellular
CuO	Bifurcaria bifurcate	05–45	Spherical	
Fe	Chlorococcumsp. MM11	20–50	Spherical	Intracellular
Ferrihyd	riteEuglena gracilis	0.6-1.0		
Pd	Sargassum bovinum	05-10	Octahedral	Extracellular
	Sargassum ilicifolium	60 - 80	Spherical	
Pt	Shewanella	05		Intracellular

5. Bioapplications of Algal-Mediated synthesis of Metallic NPs

Because they do not require any external capping or reducing agents during the synthesis of NPs, NPs manufactured from various green techniques are typically less hazardous than NPs synthesized chemically and are also devoid of dangerous compounds entangled on their surfaces. Algal species can be employed more advantageously in a variety of biomedical applications since they naturally include biomolecules that impart little to no toxicity, negating the need for the employment of hazardous chemicals during the reduction and stabilization of nanoparticles as shown in Figure 2 (González-Ballesteros et al., 2019; Bhattacharya et al., 2019). In-depth discussions of the several uses of algae-mediated NPs—mostly in biomedicine—are provided here.

Antibacterial Activity

Multi-drug-resistant bacterial strains have emerged as a result of the extensive use of antibiotics to treat bacterial illnesses. One of the biggest health problems facing the world today is finding effective and safe treatments for bacterial strains that are resistant to drugs. As NPs have shown effective and superior bactericidal action, there has been a shift in the usage of NPs as an alternative antibacterial agent. NPs have broad-spectrum antibacterial activity against both grampositive and gram-negative bacteria because they cause disruptions to the cell membrane and produce reactive oxygen species (ROS), which kill bacteria (Wang and Shao, 2017).

The antibacterial activity of the NPs made from algae against several bacterial strains has been studied. AgNPs that were biosynthesized from Padina tetrastromatica, brown seaweed, effectively inhibited the growth of Bacillus subtilis, Klebsiella planticola, P. aeuroginosa, and other Bacillus species (Rajeshkumar et al., 2012). In a different investigation, Shigella sp., S. aureus, E. coli, P. aeruginosa, and Salmonella typhi were all susceptible to the remarkable antibacterial activity of stable and colloidal-shaped AgNPs made from the aqueous extract of green sea algae Caulerpa serrulata, even at lower doses. The maximum inhibition zone of 21 mm (75 μ l) of AgNPs was noted for E. coli, whereas the minimum inhibition zone of 10 mm (50 μ L) of AgNPs was noted for S. typhi (Aboelfetoh et al., 2017).

Comparably, AgNPs made from Pithophora oedogonia aqueous extract have demonstrated possible antibacterial action against Shigella flexneri, Micrococcus luteus, B. subtilis, Vibrio cholerae, E. coli, and P. aeruginosa. P. aeruginosa had the largest zone of inhibition (17.2 mm), demonstrating the remarkable antibacterial activity of AgNPs against more resilient gram-negative rods (Sinha et al., 2015).

Moreover, S. aureus and B. subtilis growth was dramatically suppressed by spherical AuNPs made from the protein extract of the blue-green alga S. platensis (Suganya et al., 2015). Testing of AuNPs produced from Ecklonia cava and Nitzschia against E. Coli, S. aureus, P. aeruginosa, B. subtilis, Aspergillus fumigatus, C. albicans, and A. niger has shown promise in terms of antibacterial action (Venkatesan et al., 2014; Borase et al., 2017). When compared to the traditional tetracycline antibiotic, the AuNPs produced from Stoechospermum marginatum shown higher antibacterial efficacy against Enterobacter faecalis (Rajathi et al., 2012). In a different investigation, the antibacterial activity of AgNPs and AuNPs mediated by Neodesmus pupukensis was examined against a range of bacterial species. The findings indicated that Pseudomonas sp. (43 mm), E. coli (24.5 mm), K. pneumoniae (27 mm), and S. marcescens (39 mm) were the zones of inhibition of AgNPs, but AuNPs only shown efficacy against Pseudomonas sp. (27.5 mm) and S. marcescens (28.5 mm) (Omomowo et al., 2020). These results demonstrate the potential use of NPs mediated by algae as antibacterial agents in the future.

Antifungal Activity

Because antifungal medications are hard to come by and people are developing resistance to them, fungal infections are becoming an increasingly serious public health hazard. The development of novel, potent, and efficient antifungal drugs is highly motivated. NPs exhibit strong fungicidal action, suggesting that they may be a new therapy option for fungal infections (Bixler and Bhushan, 2012). Thus far, the green approach has produced the most potent antifungal drug in the form of AgNPs. According to a study, AgNPs were synthesized from Sargassum longifolium and tested for antifungal activity against a range of pathogenic fungal species, such as A. fumigatus, Fusarium sp., and C. albicans, at varying

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doses. The findings demonstrated that, in a dose-dependent manner, AgNPs dramatically suppressed the growth of every fungal strain (LewisOscar et al., 2016). In a different study, AgNPs were created using the aqueous extract of the red seaweed Gelidiella acerosa and evaluated for their antifungal properties against Trichoderma reesei, Mucor indicus, Fusarium dimerum, and Humicola insolens. The findings showed that AgNPs had significant antifungal activity when compared to a typical antifungal medication (Vivek et al., 2011). AgNPs biosynthesized from red algae Hypnea musciformis and green algae Ulva latica have been shown to be effective in inhibiting the growth of fungus strains that cause Candida parapsilosis, Candida niger, and Candida albicans (Kumar et al., 2012).

The antifungal action of AuNPs synthesized from algae has also been studied; however few studies have been published in this area. Brown seaweed aqueous extract is used to create AuNPs. Dictyota bartayresiana exhibited antifungal efficacy against Humicola insolens and the soft rot fungus F. dimerum (Balaraman et al., 2020). The antifungal potential of AgNPs and AuNPs mediated by Neodesmus pupukensis was also investigated. AgNPs were found to have antifungal potency against A. niger, A. fumigatus, A. flavus, F. solani, and C. albicans, with mycelial inhibition values of 80.6%, 57.1%, 79.4%, 65.4%, and 69.8%, respectively, compared to AuNPs' 79.4%, 44.3%, 75.4%, 54.9%, and 66.4%, respectively (Romero et al., 2010).

Antifouling Agent and Biofilm Prevention

The majority of bacteria live in biofilms, which are made up of various species like fungus and algae that communicate with one another and their surroundings (Amutha et al., 2019). In the maritime, medical, and industrial domains, biofouling—an undesired growth on submerged surfaces—poses serious health hazards and financial losses (Cheung et al., 2015). Biocides and hazardous chemicals are two examples of antifouling techniques; yet, they accumulate and contaminate the environment. Because NPs can successfully prevent bacterial adherence through NP-ligand interaction and biofilm formation on surfaces, they have been studied as alternative antifouling agents (KJ, 2017). It has been observed that AgNPs considerably inhibit the formation of biofilms against both gram-positive and gram-negative bacteria, such as Salmonella spp., Aeromonas hydrophila, S. liquefaciens, and E. coli. With an LC50 of 88.94 μ LmL⁻¹, circular AgNPs (2–17 nm) were found to be fatal to A. salina brine shrimp (Vijayan et al., 2014). AgNPs made from S. ilicifolium (33–40 nm) also showed cytotoxicity against A. salina (Supraja et al., 2016). Another study found that both macroflora and microflora were hindered in growth when phytagel and apcomin zinc chrome paint coated with AgNPs generated by T. ornate. With approximately 71.9% suppression in E. coli and 40% inhibition in Micrococcus species, the AgNPs inhibited the formation of biofilms. AgNPs can also act as selective antifouling agents for target species. For example, AgNPs killed 100% of the hatchlings of Balanu samphitrite larvae but only 56.6% of A. marina larvae (Krishnan et al., 2015).

Apart from AgNPs, CuNPs have also been employed as anti-biofilm agents against some clinical isolates of P. aeruginosa. The outcome shows that CuNPs not only hindered the formation of biofilms but also reduced the hydrophobicity of P. aeruginosa cell surfaces and extracellular polymeric materials (KJ, 2017). In a recent study, biofilm-producing bacterial strains S. epidermidis and P. aeruginosa were tested against S. myriocystum-mediated AgNPs at various concentrations (10, 20, 30, 40, and 50 μ g/mL). The maximum percentage of biofilm inhibition (67.75%) was obtained at 50 μ g/mL conc., whereas 48.34% was obtained in 50 μ g/mL AgNPs treated with S. epidermidis. In addition to P. aureginosa, AgNPs at greater concentrations (50 μ g/mL) were found to reduce the biofilm formation rate by 55.49% (Gopu et al., 2021). These results imply that algal-mediated NPs may eventually be replaced by other antifouling agent formulations, and biofilm inhibition of NPs at lowest inhibitory concentrations was associated with their suppression of motility- and biofilm-related gene expressions (Babu et al., 2020).

Anti-Cancerous Activity

The use of NPs for cancer therapy and targeted delivery of anti-cancer medications is one of the most active fields of nano-biotechnology research (Acharya et al., 2021). Recent years have seen the publication of numerous studies on the anti-cancerous properties of NPs mediated by algae. AgNPs (10 nm) produced by Sargassum vulgare shown strong anticancerous action against HeLa cells and human myeloblastic leukemic cells HL60 in a study (KJ, 2017). The non-small human lung cancer cell line (NCI-H460) was subjected to photo thermal treatment using silver nano-triangles coated with chitosan polymers produced from algae (Chit-AgNPs) (van Horssen et al., 2006). Additionally, AgNPs mediated by S. muticum have demonstrated cytotoxic effects against the MCF7 breast cancer cell line in vitro. The MCF7 cell line was treated with AgNPs at varying concentrations ranging from 3 µg/mL-50 µg/mL for approximately 48 hours. The concentration of 12.5 µg/mL produced the greatest viability rate of 100.36%. These AgNPs have caused intracellular ROS generation, which causes cancer cells to undergo apoptosis and ultimately die (Borah et al., 2020). In a different study, the cytotoxic potential of AgNPs generated by S. myriocystum against the HeLa cell line was evaluated using the MTT assay at different concentrations: 0, 2, 4, 8, 16, 32, 64, 128, 256, and 512 µg/mL. The HeLa cell line treated with AgNPs exhibited 50% inhibitory and apoptotic activities, and the concentration of AgNPs in the media improved the cell line's total cytotoxic capacities ()Gopu et al., 2020). Similar to this, different quantities (0-100 µg/mL) were used for time intervals of 24, 36, and 48 hours to determine the in vitro cytotoxicity capability of algalmediated AgNPs against the breast cancer MCF-7 cell line. AgNPs have the potential to prevent cancer, as evidenced by

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their ability to cause nuclear fragmentation, apoptosis, and cell death in breast cancer cells, with a maximal inhibitory concentration value of $20 \ \mu g/mL$ (Jena et al., 2015).

It has also been reported that substantial anti-cancerous activity against a variety of cell lines are demonstrated by algaemediated AuNPs. Strong anti-cancerous actions were demonstrated by Acanthophora spicifera-mediated AuNPs against the colorectal adenocarcinoma HT-29 cell line in one investigation. Following a 24-hour incubation period, quantities of 1.88, 3.75, 7.5, 15, and 30 µg/mL of AuNPs were administered. The MTT test was used to monitor the results. In cancer cell lines, the highest inhibitory concentration of 21.86 µg/mL was found to cause apoptosis, a loss of morphological structure, and cell shrinkage (Zhang et al., 2012). AuNPs mediated by the marine algae Chaetomorpha linum were the subject of another investigation, wherein the HCT-116 colon cancer cell line was shown to exhibit anti-cancerous potential in vitro. Following incubation with these nanoparticles, colon cancer cell lines showed dose-dependent lethal effects of AuNPs. The activation of apoptotic caspase 3 and 9 as well as the decrease of anti-apoptotic proteins including Bcl-xl and Bcl-2 were found in a series of apoptotic inductions, which unequivocally demonstrated the effectiveness of the algal-synthesized AuNPs as anti-cancer drugs (Elgamouz et al., 2020). Similarly, when compared to the anticancer cytokine tumor necrosis factor-alpha, AuNPs coated with polyethylene glycol can kill the greatest number of tumor cells (Cai et al., 2008; Kuppusamy et al., 2014). The anti-cancerous potential of NPs synthesized from algae is demonstrated by these investigations.

Nano-Bioremediation

Lately, there has been a lot of interest in the novel use of NPs to clean up contaminated locations. NPs produced by algae have been evaluated as bioremediation agents; for instance, AgNPs produced by U. lactuca photo-catalyzed the degradation of methyl orange dye when exposed to visible light. Additionally, a low dosage of U. lactuca-mediated AgNPs was found to significantly lower the population of Plasmodium falciparum, a species that is resistant to chloroquine (Kumar et al., 2013). In a study that compared AgNPs generated from Microchaete to cyanobacterial extract, the former demonstrated superior de-colorization capacity against methyl red azo dyes (Hussain et al., 2019). The catalytic activity of AuNPs produced from the aqueous extract of S. tenerrimum and T. conoides, two brown algae, was demonstrated in a different investigation against rhodamine B, sulforhodamine, and aromatic nitro compounds (Ramakrishna et al., 2016). AgNPs mediated by S. myriocystum also showed promise for photocatalytic activity against methylene blue. In less than 60 minutes, 98% of the maximum percentage of MB degradation was noted (Gopu et al., 2020). AgNPs placed into a biomatrix and mediated by Chlorella ellipsoidea shown strong photocatalytic activity in a recent study, breaking down the dangerous pollutant colors methyl orange and methylene blue. Three reduction cycles did not impair the catalytic efficiency (Sharma et al., 2019). In one study, lipid-cadmium sulfide nanoparticles were synthesized using the green alga Scenedesmus obliquus. The adsorption kinetics of Cd^{2+} ions were found to be greatly accelerated throughout synthesis and the chemisorbed monolayer (Cd²⁺) was irreversibly bonded to the algal biomass. Because of its great retention capacity, Scenedesmus therefore demonstrated to be an effective model alga for the bioremediation of Cd²⁺ ions (Nateras-Ramírez et al., 2022). This shows how different forms of algae-mediated NPs are effectively cleaning up different kinds of heavy metals, organic/aromatic compounds, and different kinds of dyes.

Biosensing

Excellent optical qualities exhibited by AuNPs produced from algae can be applied in biosensing applications, such as detecting the kind and concentration of hormones in the human body, which is very helpful in the diagnosis of cancer. The nano Au-Ag alloy synthesized from algae showed notable electro-catalytic activity against 2-butanone at room temperature, serving as a foundation for the creation of an early-stage cancer detection biosensor that can quickly identify the presence of cancerous cells at very early stages (Singh et al., 2021). A recent study assessed the colorimetric sensing of hydrogen peroxide using Noctiluca scintillans-mediated AgNPs. Hydrogen peroxide is an antiseptic and is recommended for minor skin scratches, as well as for mouth, gum, and teeth pain, as well as for whitening and oral discharge. The catalytic surface of AgNPs underwent pH, temperature, and time-dependent hydrogen peroxide breakdown, according to the results. In addition, the test revealed a color shift from brown to colorless; with hydrogen peroxide exhibiting the most pronounced color shift (Das et al., 2023). In a different investigation, the biosynthesized AuNPs produced by Hypnea Valencia shown the capacity to identify the hormone human chorionic gonadotrophin (HCG) in urine samples provided by expectant mothers during an HCG blood test (Hamida et al., 2021). Moreover, platinum nanoparticles (PtNPs), which are derived from S. myriocystum, function as biosensors to measure the body's amount of adrenaline, a hormone-based medication used to treat allergies, asthma, and heart attacks (Kumari et al., 2023).

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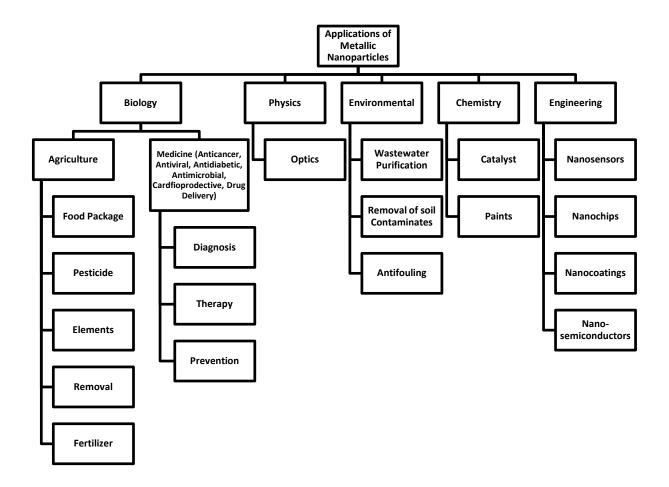


Figure 2: Applications of Metallic Nanoparticles.

6. Limitations and Future Scope

Undoubtedly, algae are great options for the environmentally friendly synthesis of nanoparticles (NPs) since they are abundant in secondary metabolites, which function as capping and reducing agents. This field, nevertheless, is still in its infancy and cannot be expanded for commercial purposes. This could be the result of a number of constraints on algalmediated NP biosynthesis, including slow reaction kinetics (taking a few days to weeks), low NP yield, poor NP morphological characteristics, improper algal strain selection, and inadequate optimization of synthesis conditions (pH, temperature, contact time, and concentration). In addition to these, there are other variables in the NP yield, and process control is one of them. Moreover, because large levels of agglomeration have been documented in some circumstances, colloidal stability is frequently a problem that requires careful consideration. The use of algae in the manufacture of NP has also been restricted by a lack of understanding of the synthesis mechanism. Therefore, more research is required to address the issues of kinetics, yield, and cell viability in order to build large-scale photo-bioreactors. Additionally, a comparative study on the physiochemical properties of NPs synthesized using conventional methods and algae represent a significant knowledge gap that the scientific community should address. Furthermore, a great deal of investigation is required to pinpoint and determine the function of particular biomolecules that are in charge of NP reduction and capping throughout the algae-mediated biosynthesis process. Furthermore, only a few varieties of NPs have been produced from algae; further research could be done in the future to create NPs such zinc oxide, silicon, palladium, and carbon-based NPs. It will be possible to synthesize algal-based NPs in a controlled and comparable manner using newly developed characterization tools. This will help to improve the properties of algal-mediated NPs for use in industry.

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7. Conclusion

Due to the lowering and stabilising abilities of secondary metabolites found in different plant extracts, it was possible to synthesise ZnO NPs utilising biological methods. It is possible to improve the quality of ZnO NPs and optimise the reaction conditions to increase the production of ZnO NPs on a wide scale using the comprehensive information about the formation mechanism of ZnO NPs that has been gathered. The biomolecule content of the extract used in the synthesis of ZnO NPs plays a significant role in the efficiency of ZnO NPs synthesised from plant extracts in agriculture, including fertility efficiency, increase in rate of germination, root development, fruits size, sugar and protein content of crops.

ZnO NPs have the potential to be used as a therapeutic agent in the treatment of cancer and microbial infections due to their ability to easily penetrate microbial cell walls and produce ROS. The amazing ability of ZnO NPs to break down inorganic waste from municipal discharge or effluents and dyes from various textile industries effluents has greatly reduced environmental pollution. To support the large-scale manufacturing of ZnO NPs from plant extracts, additional research on better ways to preserve plant extracts for a long period should be promoted.

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