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REVIEW ARTICLE

Algal biomass nanoparticles: chemical characteristics, biological actions, and applications

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Abstract
Synthesis of metallic nanoparticles (MNPs) with different forms and sizes has focused great importance due to their updated characteristics as compared to their native or natural atom counterparts. Algae are one of the most common biological entities existing autotrophically, performing around 50% of photosynthesis in the world. Different micro- and macroalgae are rich in active ingredients which are considered an appealing platform to serve as biorefineries for contriving a wide spectrum of high-value products in addition to fuels, besides their role as antioxidant, anticancer, antimicrobial, and bioaccumulators of heavy metals. Various preparation factors and parameters such as the methods used for green nanoparticle (NP) synthesis, algal extract or filtrate concentrations, pressure, pH, temperatures, contact time, particle size, other environmental conditions, and proximity greatly affect the quantity and quality of the biosynthesized NPs and their properties from algal species. The data collected from recently published articles revealed that algae (micro or macro) are an alternative material for the synthesis of NPs due to their advantages of fast growth (short life cycle), low cost, and short time for collection and harvesting, in addition to the presence of various reducing, capping, and stabilizing agents in the algal filtrate or extract which may be used to convert metal ions to nano forms such as polysaccharides, phenolics, proteins, alkaloids, and terpenoids. Therefore, algae became the important organism for green synthesis of various NPs. The algal NPs can be used with a broad spectrum of biological activities and applications such as antioxidant, antiviral, antimicrobial, and cosmetics. The current review will focus on the green synthesis of NPs using different micro- and macroalgal species and factors affecting NP preparations in addition to the biological activities of the produced NPs as antioxidant.

Keywords Green synthesis · Algae · Characteristics · Factor affecting biological activities

1 Introduction

Metal NPs (MNPs) are expressed as particles of size around or below 100 nm. NPs are classified into natural and artificial ones. Natural NPs include water colloids, fullerenes, biogenic magnetite, and so on [2, 72]. Due to their unusual optical, photoelectrochemical, electronic, and chemical properties, MNPs such as silver, gold, zinc, and iron have attracted considerable attention [48] when compared with metal ions (such as Ag^{+}, Au^{3+}, Zn^{2+}, Fe^{2+}). The nanomaterials became more available and bioreactive due to the increase of surface area and decrease in size, in addition to changes of particle surface [71].

MNPs can be synthesized using two methods: top-down (from living cells) or bottom-up (from algal culture filtrate, extracts, fractions, or pure compounds). However, algal extracts and fractions of living organisms are usually used for biosynthesis of MNPs as reported by Singh et al. [93], El-Sheekh et al. [22], and Shalaby et al. [115].

All chemicals reducing compounds are environmentally toxic and flammable. Nature has given different techniques for the synthesis of developed NPs. It has now been accounted that organic can go about as the "bio-lab" for the synthesis of MNPs at the nanometer unit utilizing a green approach [65]. Green nanotechnology from the modern biotechnological technique is used to synthesize environmentally nontoxic NPs [112]. Different forms of green NP synthesis employing plant, microorganism, and algal extracts are simple, eco-friendly, and viable

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alternatives to chemical methods [51]. The green biosynthesis steps towards the use of micro- and macroalgae have been improved in the last years because they prove to be rich in different phytochemicals such as proteins, sugars, enzymes, and pigments [13].

Algal biomass production requires a source of light (natural or artificial) and carbon dioxide (CO_2) obtained from different sources such as chimneys, air CO_2, and soluble carbonate where they have high ability to convert carbon dioxide and solar energy to organic chemical compounds. Also, macro- and microalgae (their extracts or fractions) have different secondary metabolites such as plant acids, phenolics, flavonoids, terpenoids, glycosides, and alkaloids with different biological actions to be used as food, feed, additives, drugs, pesticides, and antioxidant, antitumor, antibacterial, and antiviral agents [, 21, 42, 57, 85, 117].

Recently, algal capped and stabilized NPs have picked up far and wide consideration as being low toxicity, easily harvested, cost effective, environment-friendly, and safer to use, and prepared by green methods. There are intracellular or extracellular compounds from algae usually used for biosynthesis of different MNPs; flavonoids, sugars, phenolic compounds, and ascorbic acid in algal extracts and fractions can be used as reducing agents whereas the proteins or polysaccharides can act as stabilizing or capping agents (Figure 1) for green synthesis of various MNPs from algal species. The algal biosynthesized NPs have been used for their biomedical applications, which include antioxidant, antiviral, antibacterial, antifungal, and anticancer agents as reported by AlNadhari et al. [4]. Also, Thiruchelvi et al. [113, 118] found that the silver nanoparticle synthesized from marine macroalgae exhibited antioxidant and antimicrobial activity against both Gram-positive and Gram-negative bacteria.

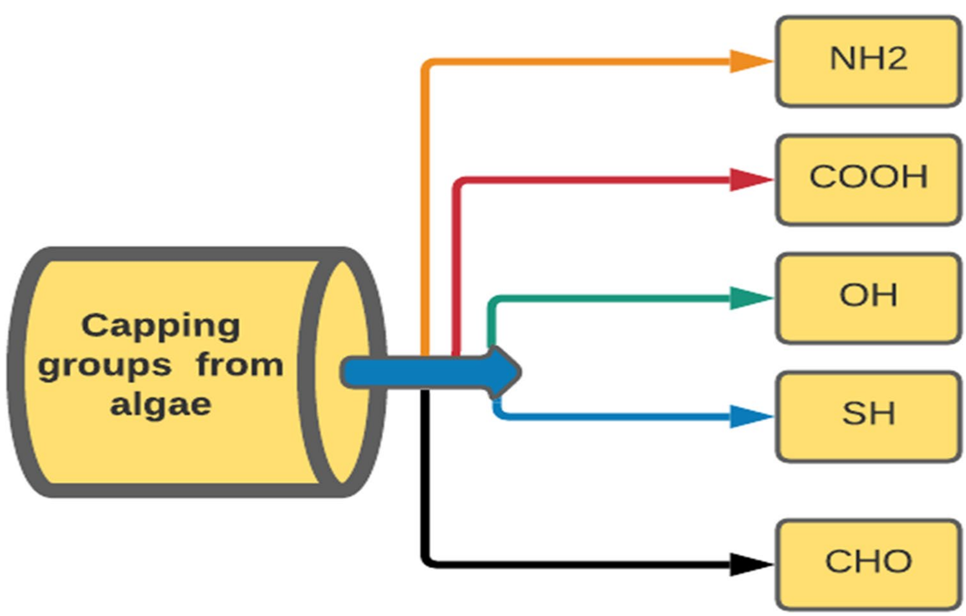
Various environmental conditions and parameters may influence the techniques used for biosynthesis, such as algal culture or extract concentrations, pressure, pH, temperature, incubation time, particle size, and use of gamma radiation. In addition, other physical methods after or during the NP biosynthesis greatly affect the quantity and quality of the biosynthesized MNPs and their characteristics as well as their applications. In addition, the characteristics of the biosynthesized MNPs are the main factor that affects their potential use in different biomedical applications and other pharmaceutical actions. Current and new studies of algal nanotechnology will give more complete skills and knowledge bases regarding different parameters that affect green production of MNPs. The most advanced technology can be used for characterization of the different MNPs for their activities and applications in variable fields and industries [112].

The aims of the current review is to highlight or focus on MNP biosynthesis using different algal species and their characteristics in addition to the biological activities of the produced NPs as antioxidant, antimicrobial, and anticancer.

2 The common laboratory methods for biosynthesis of MNPs using algae

The biosynthesis or green synthesis of MNPs started in 2009 with different techniques and various environmental conditions. Generally, MNPs were biosynthesized using the aqueous solution of the metal and algal culture or extract of different algal species under controlled conditions of temperature, pH, and stirring. The visual color change of the reaction mixture during the incubation period indicates

Figure 1 Main capping agents or groups in algal cells



the production of the appropriate MNPs, as represented in case of AgNPs (Figure 2). AgNPs could be produced using brown seaweed *Saccharina cichorioides* and *Fucus evanescens* [107], using marine green alga *Caulerpa racemosa* [41], red alga *Portieria hornemannii* [23], and red seaweeds *Corallina elongata* and *Gelidium amansii* [31] under specific controlled conditions. Algal crude extracts contained different chemical compounds which can be used for the reduction of metal ions to MNPs. These compounds may include phenolic compounds, carboxylic acid compounds, and polysaccharides.

3 Factors affecting AgNP production by algae

Several published articles have various environmental conditions and factors that were used for NP production, such as concentration of extract, pH degree, pressure, temperature, incubation period, particle size, and other reaction conditions which highly affect the quality of the biosynthesized MNPs and their characteristics and applications. Moreover, the properties of the produced MNPs affect their potencies in various fields such as medicine or drug delivery and other environmental applications. The present section illustrates major parameters affecting the green synthesis of MNPs by algal species. New and previously published data on algal nanotechnology will provide high skills and knowledge base regarding different factors that influence biosynthesis of MNPs. Meanwhile, the most recent technology can be used for characterization of the MNPs for their actions and applications in different fields [102]. The following are the parameters influencing the green synthesis of MNPs from various algal extracts and species

3.1 Preparation methods

There are different methods used for green synthesis of MNPs from algae (micro and macro); among these methods or techniques are (a) physical techniques and (b) chemical and (c) biological methods. Each procedure has its specific advantages and disadvantages. However, biological methods (for example, use of algal extracts or cultures) for synthesis of AgNPs are nontoxic, eco-friendly, and more acceptable than other (physical and chemical) methods as reported by Vadlapudi and Kaladhar [103].

3.2 Dispersing agent

The synthesized MNPs using aqueous polymer have a narrow range of diameters around 10 nm. The other nanosilver particles synthesized using a low molecular weight (LMWt) dispersing agent have a reduced NP size and a slighter type of distribution than aqueous polymer–based AgNPs [70].

3.3 Extract concentration

There is a great correlation between the concentration of algal extract and surface plasmon resonance (SPR) band intensity of synthesized MNPs; the results reported that the suitable algal concentration ranged from 10 to 20 %. Several published articles found that reducing agents, dispersants, and various types of amine groups affect the shape and size of the produced NPs [45].

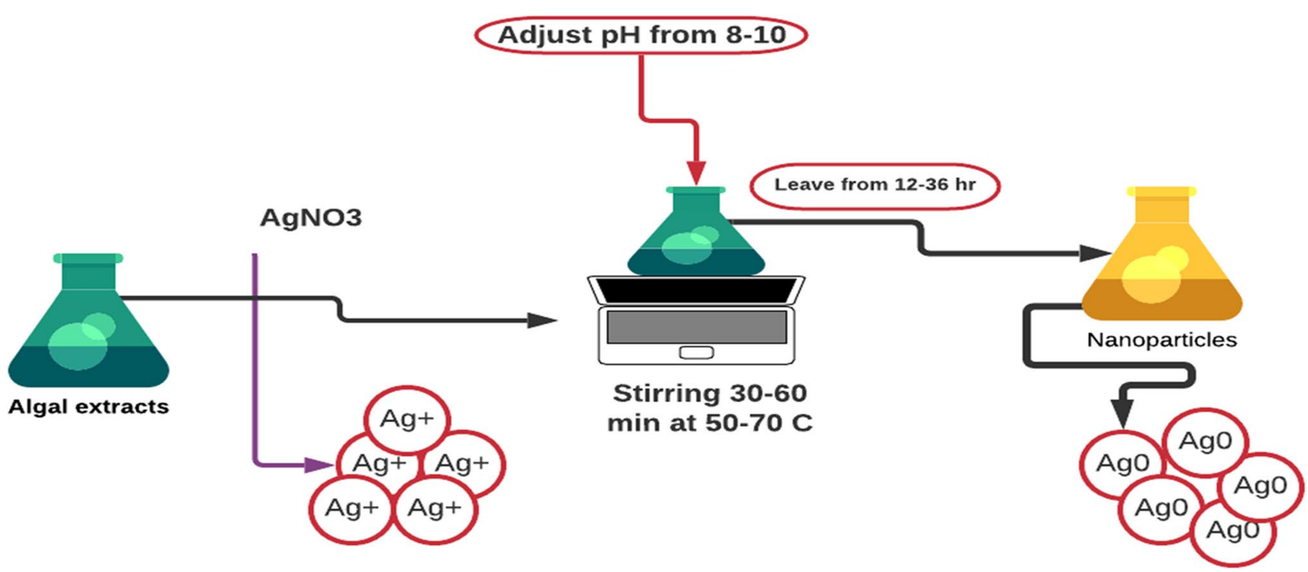


Figure 2 The main process for green synthesis of AgNPs using algal extracts

3.4 Temperature

Three common methods for preparation of NPs are usually used for synthesis of MNPs (physical, chemical, and biological).

Physical methods need a very high temperature (exceed 350 °C), whereas chemical methods need a temperature degree lower than 350 °C. However, the synthesis of MNPs by green synthesis needs temperatures below 100 °C as described by Rai et al. [76]. Also, Jiang et al. [39] reported that temperature can highly affect the synthesis, growth, shape, and distribution of particle sizes. The same authors mentioned that (i) a low temperature decreases the formation of NPs and led to increasing the time needed to complete reducing of the reaction. (ii) With an increase in the temperature to 55 °C, the rate of synthesis increased,in addition, it led to an increase in the particle size. (iii) At an elevated temperature of more than 60 °C, the reaction became more active in reducing silver ions. Due to these phenomena, the biosynthesized NP size would become very smaller with high temperatures and a larger size can be produced at low temperature. In general, exposure to high or low temperature (cooling) of the biosynthesis reaction will have an influence on the surfactant adsorption/desorption, complexing stability, biosynthesis rate, and shape and size of produced NPs. However the updated results stated that NPs can be synthesized at a temperature of 25 °C using chemical, biological, and physical methods [96].

3.5 Pressure

One of the important factors which control the green synthesis of various MNPs is the time needed or the rate of metal ions reduction using algal extracts. It is much faster at normal pressure. Pressure affects the shape and size of the synthesized MNPs as a condition described by Tran et al. [101].

3.6 Extract composition

The active ingredient contents of algal extracts such as proteins, enzymes, phenolics, flavonoids, and sugars in addition to their reducing agent content, type of the algal species, the type of solvent used for extraction, extraction methods, and culture conditions are very important factors exerting an effect on MNP biosynthesis and its properties [74].

3.7 Contact time

An increased incubation period or reaction time led to rapid biosynthesis of MNPs as reported by Darroudi et al. [16], who found that the type and characteristics of synthesized MNPs using algal cells or algal extracts are greatly affected by time during which the reaction solution is incubated.

3.8 pH

pH is one of the important factors effecting the biosynthesis of MNPs, using green technology methods. Various published articles emphasized that the pH degree of the metal solution affects the size and texture of the biosynthesized MNPs [6, 24, 112]. Also, the AgNP size can be modified by changing the pH degree of the metal solution. The same results obtained by Soni and Prakash [96], who reported that the pH of the reaction solution had an influence on the shape and size of synthesized MNPs by algal species.

In this regard, Parial et al. [73] studied the effect of pH on the shape of NPs. They reported that all the three alga strains, *Phormidium valderianum*, *Phormidium tenue*, and *Microcoleus chthonoplastes*, were able to produce NPs intracellularly. Only *Phormidium* sp. could produce gold nanospheres (AuNPs) with a 15-nm diameter at pH 5 and triangular NPs with 24 nm at pH 7 and hexagonal NPs with 25 nm at pH 9.

Alqadi et al. [5] mentioned that the MNPs which were synthesized at high pH (ranging 10 and 11) were unique with a more regular and smaller size when compared to NPs synthesized at a low pH degree. The average radii of the produced particles ranged 43.00 and 32.00 nm, respectively, and the shape of the produced AgNPs is spherical. The same authors reported that increasing the pH degree led to the formation of spherical NPs when compared with the AgNP shape at low pH. The results indicated the formation of rods and triangular shapes, and this result may be due to poor balance between growth processes and nucleation.

Figure 3 summarizes the effect of different pH values of the reaction solution on the size of MNPs as reported by Soni and Prakash [96].

4 Properties of MNPs produced by algae

The characteristics of algal MNPs are usually evaluated using different spectroscopic, surface area analysis, diffractographic, and microscopic techniques as described by Khanna et al. [45] and Farrokheh et al. [110].

The following points summarize the important indicators and confirmation of MNPs synthesized using algal cultures or extracts.

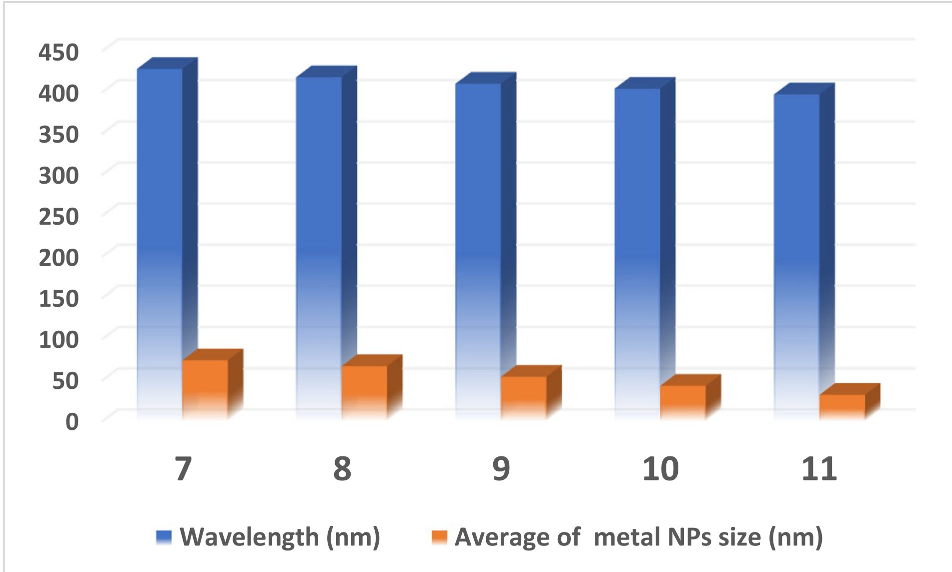


Figure 3 Effect of pH on the size and wavelength (nm) of produced MNPs

4.1 First indicator: color change of the reaction mixture

Biosynthesis of MNPs using algal cells or algal extracts (as reducing agents) was ensured by the change of color from green, colorless, or light yellow to dark yellowish or brown color [84]

4.2 Second indicator: UV-Vis spectrophotometric absorption of NPs

UV-Vis spectroscopy is usually used to confirm the different types of NP production by evaluating plasmon resonance and measuring the collective oscillations of conduction band electrons according to electromagnetic waves. These biosynthesized MNPs were characterized by UV-Vis spectrophotometry that indicated the formation of MNPs at the absorbance ranging 390 to 450 nm [23]. Other studies were performed by Danagoudar et al. [15] and Akpomie et al. [109], who found that there are characterization peaks at 400 nm. The intensity of absorption of NPs was increased with silver nitrate ($AgNO_3$) concentration and reached the maximum at 3 mM, and this reflects the bioreduction process completion. However, the absorption peak did not change from 400 nm and did not shift to other wavelengths upon $AgNO_3$ incubation with green extract. This result may be correlated with the non-agglomeration of MNPs. This result was in agreement with the observations of Hulikere and Joshi [33]. In addition, the same investigations reported that the extinction peak of AgNPs showed a blueshift after the addition of reducing agents as a result of an increased free electron number. The UV-Vis spectrum of different MNPs produced by algae may exhibit an absorption peak at 490 nm. The synthesized MNPs capped with active molecules are well dispersed in reaction and stable up to 3 months as recorded by retention of a brownish solution color [7].

4.3 Third indicator: determination of the reductant (by FTIR)

Fourier transform infrared (FTIR) spectroscopy evaluation of fine specimens was employed to investigate attainable active groups which interact between metal solution and algal extracts. The Fourier transform infrared spectroscopy study was implemented to detect and identify the biomolecules responsible for reduction of silver ions (Ag^+) into AgO and appearance of any modification in group absorption peaks [23]. Also, FTIR, for example, showed that for both AgNPs and $AgNO_3$, the aldehyde groups on the algal cell surface were oxidized to –COOH groups by Ag^+ ions, irrespective of the presence of extracellular polysaccharides in different algal cells [108].

A study implemented by Sathishkumar et al. [82] has revealed that amino, amide, and carbonyl groups showed a tendency of binding with metal particles, thus forming a layer on the MNPs, which led to their agglomeration and stabilization. Different active or functional groups in algal extract may influence the interaction of MNPs with proteins, peptides, or carbohydrates. In the same context, Xie et al. [106] reported that carboxyl and hydroxyl groups from the extract of green microalga *Chlorella vulgaris* are involved in the biosynthesis of AgNPs.

Table 1 Characteristics of some MNPs biosynthesized by different algal species (macro- and microalgae and cyanobacteria)

Algae species	Type of NP	Shape of NP	Size of NP (nm)	References
Anabaena sp. L31	ZnO	Spherical	80	Singh et al. [92]
Microcoleus sp.	Ag	Spherical	44–79	Sudha et al. [98]
Leptolyngbya boryana	Au	Octahedral	Less than 10 μm	Lengke et al. [52]
Arthrospira platensis	Au core-Ag shell	Spherical	17–25	Govindaraju et al. [26]
Chlamydomonas reinhardtii	Ag	Rounded and rectangular	5–15	Barwal et al. [12]
Chlorella vulgaris	Au	Nanoplates	-	Xie et al. [106]
Chlorococcum sp.	Fe	Spherical	20–50	Subramaniyam et al. [97]
Caulerpa racemosa	Ag	Spherical and triangular)	5–25	Kathiravan et al. [41]
Ulva (Enteromorpha) compressa	Ag	Spherical	40–50	Dhanalakshmi et al. [19]
Ulva reticulata	Ag	Spherical	40–50	Dhanalakshmi et al. [19]
Padina gymnospora	Au	-	53–67	Singh et al. [91]
Sargassum cinereum	Ag	Spherical	45–76	Mohandass et al. [64]
Gracilaria dura	Ag	Spherical	6	Shukla et al. [88]
Lemanea fluviatilis	Au	-	5–15	Sharma et al. [86]

4.4 Fourth indicator: zeta potential

The stability and charge of the NP surface are determined indirectly using zeta potential analysis by a Zetasizer. The zeta potential is measured as the difference between the outer Helmholtz plane and the surface of shear.

The negative results or value of the zeta potential reported the efficiency of the reducing or capping chemical compounds of algal extracts in AgNP stabilization by given negative charges that keep all the particles away from each other as found by Haider and Mehdi [29]. Table 1 illustrates the characteristics of MNPs prepared from different algal species.

5 Biological actions of MNPs produced from different algal species

The NPs biosynthesized using green synthesis are used in the food, medicinal, pharmaceutical, and agricultural fields and have a great deal of interest. Micro- and macroalgae are a platform for the biosynthesis and release of diverse MNPs; this is due to the presence of different active compounds such as proteins, sugars, phenolics, alkaloids, and terpenoids which act as antioxidant, anticancer, antimicrobial, and antiviral in their cell extracts (Figure 4 and Table 2) that act as biocompatible reductants. The common algal species *Chlorella* spp. (as

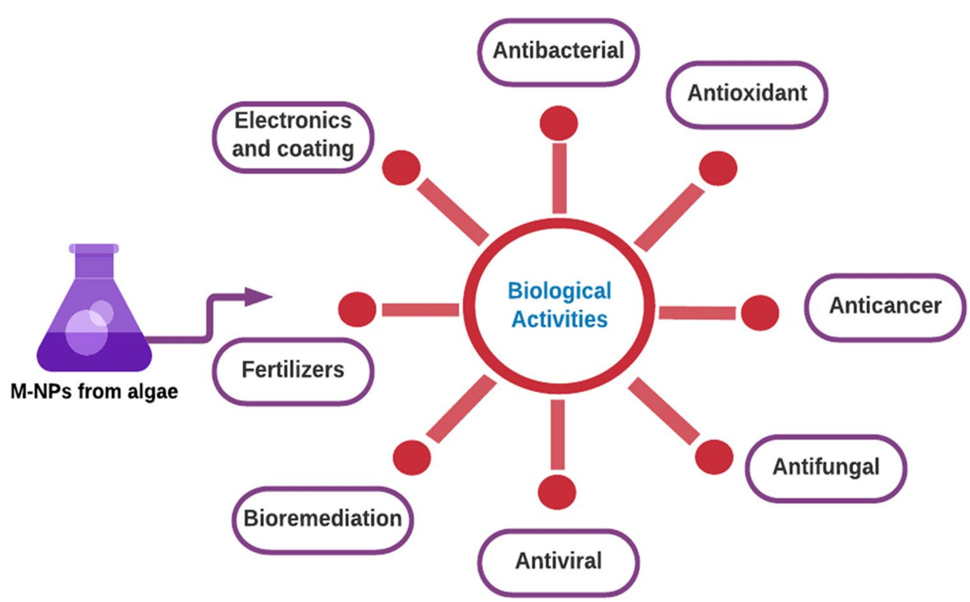


Figure 4 The biological activities of algal based NPs

Table 2 Biological activities of some NPs produced from algal species

Algal species	Type	Capping agents	Biological activities	References
Gelidiella acerosa	Silver	Phenolic compounds	Antibacterial	Thiruchelvi et al. [113, 118]
Ulva lactuca	Silver	Phenolic compounds, amines, and aromatic rings	Photocatalytic degradation	Kumar et al., [49]
Ulva lactuca	Silver	Polyphenol	Malaria control	Murugan et al. [68]
Gracilaria corticata	Silver	Polyphenols and tannins	Antifungal activity	Kumar et al., [49]
Corallina officinalis	Gold	Hydroxyl and amino functional groups	Anticancer activity	Khanna et al. [45]
Sargassum wightii	Silver	Oxidation of alcoholic and carboxylic acid groups	Antibacterial activity	Govindaraju et al. [27]
Sargassum myriocystum	Zinc oxide	Alginic acid, ascorbic acid, protein, carbohydrates, flavanoids, tannins, mannitol, and lipids	Antibacterial activity	Nagarajan et al. [69]
Turbinaria conoides	Silver	Polyphenols, polysaccharides, primary amines	Antimicrobial	Rajeshkumar et al. [79]
Padina gymnospora	Platinum	Sulfated polysaccharide	Hemolytic assay	Shiny et al. [87]
Sargassum swartzii	Silver	Alcohol, carboxylic, and amide group	Anticancer activity	Dhas et al. [20]
Fucus vesiculosus	Gold	Hydroxyl groups in polysaccharides of the algal cell wall, extracellular synthesis	Biogenic mechanisms of gold deposition involved in the formation of natural deposits	[63]
Sargassum polycystum	Silver	Hexadecane, hexadecanoic acid, cis-9-octadecanol, 1-eicosanol, octadecanoic acid	Gram +ve: *S. aureus*	[100]
Padina tetrastromatica	Silver	Bromoalkanes engage in recreation the foremost role in the NP synthesis	Gram +ve: *Bacillus* spp. *B. subtilis*	[78]
Sargassum longifolium	Silver	Extracellular, terpenoids with aldehyde, ketone, carboxylic acid groups, carbonyl group from amino acid residues that form the NP capping	Anticancer against Hep 2 cell line	[18]
Turbinaria ornata	Silver	Organic moieties as stabilizing agents	Gram +ve: *B. litoralis*, Bacillus sp., *Micrococcus* sp., *Corynebacterium* sp., *S. aureus*	[47]
Turbinaria conoides	Gold	Biochemical material	High antibacterial activity against *Streptococcus* sp., and medium for *B. subtilis* and *K. pneumoniae*	[79]
Cystoseira baccata	Gold	Bioreduction by polyphenols and polysaccharides; capping by proteins; metal complexation by sulfonic groups from polysaccharides	Cytotoxic effect against human colon cancer cell lines HT-29 followed by Caco-2; biocompatibility with healthy cell line PCS-201-010	[25]
Kappaphycus alvarezii	Gold	Extracellular, polyphenol compounds	Antibacterial against *Pseudomonas fluorescens*, *S. aureus*	[77]
Urospora sp.	Silver	Hydrogen-bonded hydroxyl group, carbonyl and alcoholic group	Gram +ve: S. aureus, B. subtilis; Gram -ve: *E. coli*, *P. aeruginosa*, *K. pneumoniae*	[99]
Ulva lactuca	Silver	Release of protein molecules	Anticancer: Hep2, MCF7 and HT29 cancer cell lines	[17]
Gelidiella acerosa	Silver	Aromatic compound or alkanes or amines	Antifungal against *Humicola insolens*, *Fusarium*	[105]
Chlorella vulgaris	Silver	Gold shape-directing protein of 28 kDa	Optical coatings and hyperthermia of cancer cells	[106]
Spirulina platensis	Gold	Extracellular; biomolecules (amino, carboxylic, phosphate, thiol)	Pharmaceutical technological	[40]
Phormidium spp.	Gold	Cytoplasmic protein moieties	Antioxidant activity by DPPH, interaction with DNA, biolabeling	[67]
Anabaena spp.	Gold	Protein or cellular enzymes	Self-reproducing bioreactor for in vivo biosynthesis	Khanna et al. [45]

Table 2 (continued)

Algal species	Type	Capping agents	Biological activities	References
Tetraselmis kochinensis	Gold	Intracellular, reduction by enzymes present in the cell wall and cytoplasmic membrane	Catalysis, electronics, and coatings	Khanna et al. [45]
Euglena gracilis	Silver	Primary amines of proteins	Comparison of in vitro and inB203 vivo both	[54]
Plectonema boryanum	Pd	Organic materials	First viable alternative method	[53]
Phormidium tenue NTDM05	CdS	C-phycoerythrin, thiol groups partial capping along with biological molecules	Biolabeling	[66]
Sargassum myriocystum	ZnO	Fucoidan water-soluble pigments	Natural nanomedicine against microbial infection	[69]
Chlorococcum sp. *MM11*	Fe	Carbonyl and amine bonds from polysaccharides and glycoproteins present in the algal cell wall	Remediation of toxic Cr(VI)	[97]
Padina tetrastromatica	Silver	Alkanes	Gram-positive *Bacillus* spp., *B. subtilis*	Rajeshkumar et al. [78]
Sargassum longifolium	Silver	Terpenoids	Anticancer activity	Devi et al. [18]
Turbinaria ornata	Silver	Organic compounds	Antibacterial activity against Gram-positive strains	Krishnan et al. [47]
Sargassum sp.	Au	Carbonyl, hydroxyl, amine functional groups and tannic materials	Against aging	[56]
Sargassum wightii	Au	Biotransformation using algal species	Development of bioprocess for synthesis	[90]
Ecklonia cava	Au	Primary amine group, hydroxyl group	High antimicrobial activity against E. *coli* and *A. niger*, biocompatible as nontoxic for HaCaT cell lines	[104]
Plectonema boryanum	Pt	Polysachharides rich with uronic acids subunits, which, through their carboxyl groups	First study as an alternative method to abiotic chemical methods	[52]
Gracilaria edulis	ZnO	Quinines	Anticancerous against PC3 cell lines	[75]
Sargassum muticum	Fe_3O_4	Sulfated polysaccharides in the reduction process and the stabilization, extracellular synthesis	High functional bioactivity	[61]
Plectonema boryanum UTEX 485	Silver	Utilizing nitrate by reducing nitrate to nitrite and ammonium, which is fixed as glutamine before death	Temperature-dependent size control of NPs	Lengke et al. [53]
Microchaete NCCU-342	Silver	Cellular metabolites	Degradation of azo dye methyl red	Husain et al. [35]

microalga) and *Sargassum* spp. (as macroalga) have been extensively explored for the synthesis of NPs which have antimicrobial properties, and can potentially substitute conventional antibiotics. Characterization of NPs synthesized from algae has been done using advanced spectroscopic, diffractographic, and microscopic techniques such as UV-Vis FTIR, DLS, XPS, XRD, SEM, TEM, AFM, HRTEM, and EDAX [45].

MNPs synthesized from various algal species used a multidisciplinary approach resulting from the investigational use of NPs in different biological systems [37] and [45].

Nowadays, a lot of scientists focus on nano-drug production, as they provide tools for a great number of drug delivery systems due to their pharmacokinetics and biodistribution behaviors. They reported to have antibacterial [45, 116], anticancer [28, 45], and antifungal activities [, 8, 45]. The antimicrobial, antioxidant, and anticancer activities in addition to NP toxicity are discussed in the following sections.

5.1 Antioxidant activity

The production and accumulation of various oxidative stresses in our body leads to different diseases in the human body. The reactive oxygen and nitrogen species (ROS and RNS) free radicals through inflammatory action cause various health problems in the human body due to normal body metabolic acidity.

The radical-scavenging activity of the green-synthesized NPs was carried out using DPPH radical assay. The MNPs such as AgNPs showed high antioxidant activity as reported by Kharat and Mendhulkar [46],this action was correlated with the presence of phenolic compounds associated with the MNPs which are responsible for antioxidant activity. The same author in a previous study showed the presence of the same phenolic compounds in the *Penicillium citrinum* CGJ-C1 extract. So, the recorded antioxidant actions might be due to the presence of phenolic compounds in green extracts. The same results were recorded by Li et al. [55], who reported that the biosynthesized MNPs have better antioxidant actions with low antioxidant activity when compared with ascorbic acid as the natural antioxidant standard. So, the biosynthesized AgNPs are still promising as a suitable antioxidant agent. The antioxidant effect may be due to the adsorption of some biochemical compounds like phenols or peptides on the spherical and nanometal particles.

The antioxidant action of AgNPs produced using *Microsorum pteropus* of methanolic extract was evaluated by Chick et al. [14], who mentioned that MNPs have high antioxidant properties against the DPPH method by an IC_{50} value of 47.0 ppm and H_2O_2 assay by an IC_{50} value of 35.8 ppm, when compared with natural extract, which recorded 17.4 and 11.5 ppm, respectively. Another study carried out by AlNadhari et al. [4] found that the high antioxidant activity of AgNPs is greatly interlinked with the brown macroalga *Ecklonia cava* extract synthesis that still on the upper layer of the AgNP flecks. Inhibition of free radicals of *Ecklonia cava* extract and biosynthesized AgNPs was consistent with making use of the current antioxidant assay (DPPH).

The antioxidant potential of synthesized AgNPs using aqueous extract of *Trichodesmium erythraeum* at 500 mg/mL was 77.01 % against DPPH and 67.5 % against deoxyribose assay. However, it recorded 52.77 % with ABTS assay and 88.12 % against nitric oxide radical-scavenging assays [82].

5.2 Antimicrobial activity

Blue-green algal strains such as *Spirulina* spp. and *Microcoleus* spp. have high ability to biosynthesize metal NPs such as AgNPs with a broad spectrum as antibacterial activity against both Gram-positive and Gram-negative bacteria. AuNPs and Ag-Ngold and AgNPs from cell members of Chlorophyceae such as *Ulva* and *Chlorella* showed great potential against bacteria, fungi, and protozoa [45].

The antibacterial action of AgNPs has received a lot of studies by Hamouda et al. [31] and Rahman et al. [114]. They reported that capping AgNPs using red macroalgae have been shown to increase antibacterial action against pathogenic bacteria when compared to non-capping AgNPs. The same data and results were recorded by Thiruchelvi et al. [113, 118].

Also, Baker-Austin et al. [10] found that AgNPs have different and potential applications in many sectors including medicine and biology. They reported that AgNPs can be used as antibiotic substitutes. Moreover, Abdel-Raouf et al. [1] found that the AgNPs synthesized by marine red alga *Gelidium amansii* have high antibacterial activity for prominent microfouling bacteria.

The conjugation between AuNPs with antibiotics can improve the antimicrobial or antibacterial effect of NPs [89].

The antimicrobial activity of the green-synthesized AuNPs was studied by Lee et al. [51] against Gram-positive and Gram-negative bacteria using the disk diffusion assay. They found that the highest antimicrobial activity was recorded against *Staphylococcus aureus* by a 16-mm inhibition zone, followed by *Escherichia coli* with 14 mm and *Bacillus subtilis* with 12 mm. The mode of action of the activity of gold ions on the mentioned bacterial strains is partially known. Hamouda et al. [30] mentioned that the positive charge on gold ions is necessary for their antibacterial activity through electrostatic reaction between the negative-charged cell membrane of the microorganism and positively charged NPs. Another mode of action is that the AuNPs led to formation of holes in the microbial cell walls by increasing the cell wall permeability resulting in leakage of the cell contents and leading to cell death.

The synthesis of AgNPs from *Padina tetrastromatica* efficiently inhibited the growth of *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Klebsiella planticola*, and other *Bacillus* sp. In other studies, AgNPs synthesized from *Caulerpa serrulata* (marine alga) displayed high antimicrobial activity at low concentrations against *Shigella* sp., *S. aureus*, *E. coli*, *P. aeruginosa*, and *Salmonella typhi*. Additionally, AgNPs using *Pithophora oedogonia* watery concentrate have found possible antimicrobial activity against *E. coli*, *Micrococcus luteus*, *S. aureus*, *B. subtilis*, *Vibrio cholerae*, *P. aeruginosa*, and *Shigella flexneri* [94]

The antimicrobial action of algal synthesized and extracted Cu and AgNPs was investigated using both Gram-positive and Gram-negative bacteria and fungi with the use of the agar diffusion assay. The algal native extracts did not record any inhibition zone; however, the synthesized NPs using algal culture recorded high antimicrobial activity against both pathogenic bacteria and fungi. The observed diameters of inhibition zones were as follows: *Staphylococcus aureus*, 22 mm; *Klebsiella pneumoniae*, 20 mm; *Escherichia coli*, 18 mm; and *Pseudomonas aeruginosa,* 17 mm, as reported by AlNadhari et al. [4].

The antimicrobial action of algae-coated selenium nanoparticles (SeNPs) against *Vibrio harveyi* was improved with MIC of 200 µg/mL compared to uncoated SeNPs, which recorded MIC of 400 µg/mL [62].

5.3 Anticancer activity

The MNPs produced using green materials showed higher cytotoxicity in the tumor cells compared to the normal cell; among these MNPs, the AgNPs recorded lower cytotoxicity in HEK-293 (the noncancerous cell line), compared to cancer cells as reported by Danagoudar et al. [15]. This work suggested that the synthesized AgNPs using green materials have more cytotoxicity against tumor cells than the non-tumor cells and suggested that AgNPs can be a best source for anticancer drug production. Other studies by Hu et al. [32] and Balakumaran et al. [11] and Janakiramana et al. [38] observed that myco-NPs can led to cytotoxicity by inducing the apoptosis of tumor cells. These findings obliged us to hypothesize that these AgNPs may act as cytotoxic agents by supporting the apoptosis process in tumor cells.

AlNadhari et al. [4] assessed the anticancer activity of AgNPs produced by using *Ecklonia cava* by using a tumor cervical cell line. IC_{50} of the silver nano-sized flecks was recorded as 59 µg/mL.

Moreover, AgNPs prepared by *Corallina elongata* and *Gelidium crinale* had a high antitumor action against Ehrlich ascites carcinoma (EACC) as mentioned by Khalifa et al. [43]. In addition, the results obtained by González-Ballesteros et al. [111] revealed that AgNPs have a significant biomedical application for tumor immunostimulant treatment. The green-synthesized AuNPs using algal species showed a concentration dependent inhibitory activity on growth of colon cancer cells. The median inhibition concentration was 15 mg/ mL, and the maximum inhibition was >75% of the cell death obtained with 25 mg/mL [89].

The cancer activity of the AuNPs was assessed against breast cancer (MCF-7), breast cancer (HTB-22) and gastric carcinoma (NCI-N87), and gastric cancer cells (CRL-5822) at 10, 50, and 100 ppm concentrations. The obtained data revealed a direct concentration-response relationship. The anticancer effect increased at higher NP concentrations. At 100 ppm, the highest inhibitory activity was recorded in MCF-7 (61.2%) and NCI-N87 (95.6%). The minimum inhibitory activity observed on MCF-7 (8.6%) is shown by Lee et al. [51].

Sathishkumar et al. [82] reported that increasing the concentrations of algal NPs led to reducing the viability of tumor cells and increasing their potential application in cancer treatment.

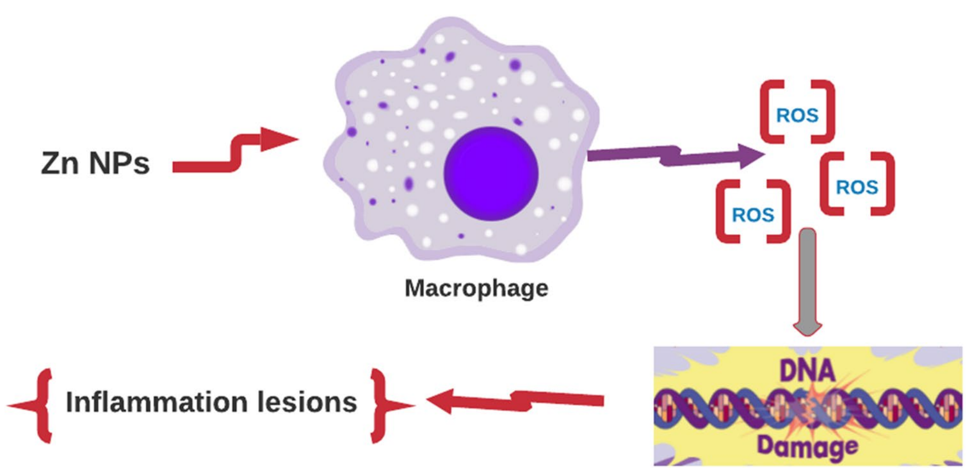


Figure 5 The cytotoxicity of zinc-based NPs

The cell viability assay on two cell lines revealed that both the algae-coated and uncoated SeNPs recorded toxicity action neither on the human lymphocyte nor on the shrimp hemocyte at 25 ppm after incubation for 48 h [62].

5.4 Toxicity of MNPs

Until now, there are no enough information and guidelines about the side effects of NPs on the environment and human health [83]. Preliminary studies showed that MNPs can affect biological functions at the cellular, organ, tissue, and protein levels of different living organisms. The side effects of diverse NPs may be due to their chemical composition, solubility, surface structure, small size, and aggregation behavior [71]. In vitro cytotoxicity evaluation has revealed that Zn-based NPs have greater toxicity (Figure 5) when compared to Cu and AgNPs, while Fe and Ti NPs possess the least amount of toxicity [81]. These MNPs have a carcinogenic effect which is triggered by the reactive oxygen species (ROS) produced by macrophages. It leads to nucleic acid damage and induction of inflammatory lesions [60]. Also, Khanna et al. [45] found that the distribution of titanium dioxide NPs causes genetic denaturation and DNA damage, which was correlated with the site of reactive oxygen release in the living cell.

However, the cytotoxicity assay of silver and gold NPs against a human fibroblast cell line (WI-38) for 24 h and 3 days was studied by Khan et al. [44], who showed that they were completely safe towards this type of cells. Therefore, these biosynthesized NPs could be considered promising supplementary targeting materials.

6 Conclusion

The consumption of MNPs around the world is expected to increase according to their increasing manufacturing demand. It may be used in different fields such as agriculture, medicine, pharmaceuticals, and industries. Algae are one of the most common biological entities existing autotrophically, performing around 50% of photosynthesis in the world. Different micro- and macroalgae are rich in active ingredients which are considered an appealing platform to serve as biorefineries for contriving a wide spectrum of high-value products. In addition to green synthesis of NPs which can be used as antioxidant, antimicrobial, anticancer, bioaccumulators, etc., they are not cytotoxic and are eco-friendly to the environment. However, still there is a need to find out the details of other NP applications, and the best approach regarding a high product yield, so that the green approach using micro- and macroalgae can be performed or applied at a larger scale.

Declarations

Conflict of interest The authors declare no competing interests.

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