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ALGAE AS A SOURCE FOR SYNTHESIS OF NANOPARTICLES – A REVIEW

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Abstract-Nanoparticles (NPs) can be broadly classified into two groups namely, organic nanoparticles (which include carbon nanoparticles) and inorganic nanoparticles (include magnetic nanoparticles, noble metal nanoparticle and semiconductor nanoparticles). Literatures revealed that the NPs synthesis using marine plants, microorganisms and algae as source has been unexplored and underexplored. Pharmacological studies, cure for antiviral diseases have been obtained from marine, source which mainly refers to the microalgae and macroalgae in the aquatic environment for the discovery of various other antiviral bioactive compounds. Presently, the researchers are looking into the development of cost-effective procedures for producing reproducible, stable and biocompatible silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs). AgNPs and AuNPs play a vital role in nanobiotechnology as biomedicine against drug-resistant bacteria.
Keywords: Algae, bioactive compounds, gold nanoparticle, silver nanoparticle.

Introduction

Nanotechnology refers to an emerging field of Science that includes synthesis and development of various nanomaterials. Nanoparticles (NPs) can be defined as a small object that behaves as a whole unit in terms of its transport and properties. They are three types, i.e., natural nanoparticles, incidental nanoparticles and engineered nanoparticles. Presently, different metallic nanomaterials are being produced using copper, zinc, titanium, magnesium, gold, alginate and silver. Nanoparticle are being used for diverse purposes, medical treatments, industry production such as solar and oxide fuel batteries for energy storage to wide incorporation into diverse materials of everyday use such as cosmetics or clothes (Dubchak *et al*., 2010). Naturally occurring biomolecules have been identified to play an active role in the formation of nanoparticles with distinct shapes and sizes thereby acting as a driving force for the designing of greener, safe and environmental protocols for the synthesis of nanoparticles. There is a growing need for green chemistry synthesis of nanoparticles using biological systems since it is less toxic, cheap and environmental friendly (Singaravelu *et al*., 2007). The present review summarizes the synthesis and application of algal nanoparticles.

Synthesis of NPs using algae

Synthesis of nanoparticles using algae can be performed in three important steps, (1) preparation of algal extract in water or in an organic solvent by heating or boiling it for a certain duration, (2) preparation of molar solutions of ionic metallic compounds and (3) incubation of algal solutions and molar solutions of ionic metallic compounds followed either by continuous stirring or without stirring for a certain duration under controlled conditions (Thakkar *et al*., 2010; Rauwel *et al*., 2015). The synthesis of nanoparticle is dose dependent and it is also related to the type of algae used. There are a variety of biomolecules responsible for the reduction of metals which include polysaccharides, peptides, and pigments. Stabilizing and capping the metal nanoparticles in aqueous solutions is done by proteins through aminogroups or cysteine residues and sulphated polysaccharides (Singaravelu *et al*., 2007). Synthesis of nanoparticles using algae takes comparatively shorter time period than the other biosynthesizing methods (Thakkar *et al*., 2010; Rauwel *et al*., 2015). So far, several seaweeds, namely *Chaetomorpha linum* (Kannan *et al*., 2013), *Enteromorpha flexuosa* (Yousefzadi *et al*., 2014), *Fucus vesiculosus* (Mata *et al*., 2009), *Turbinaria conoides* (Rajeshkumar *et al*., 2012), *Sargassum wightii* (Singaravelu *et al*., 2007), *Stoechospermum marginatum* (Rajathi *et al*., 2012), *Ulva faciata* (El-Rafie *et al*., 2013) and *Ulva reticulata* (Sudha *et al*., 2013) have been used for the synthesizing AgNPs of different sizes and shapes.

Marine algae are meagrely explored for the synthesis of NPs. *Chlorella vulgaris* has strong binding ability towards tetrachloroaurate ions to form algal-bound gold reducing into Au(O). Approximately, 90% of algal-bound gold attained metallic state, and the crystals of gold were accumulated in the inner and outer parts of cell surfaces with tetrahedral, decahedral, and icosahedral structures (Jianping *et al*., 2007). *Spirulina platensis* has been utilised for

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the extracellular synthesis of gold, silver, and Au/Ag bimetallic NPs (Chakraborty *et al*., 2009). Senapati *et al*. (2012) reported the intracellular production of gold nanoparticles using *Tetraselmis kochinensis*. The biomass of the brown alga *Fucus vesiculosus* was reported for the reduction of Au (111)-Au(0) (Mata *et al*., 2009). In addition to seaweeds, microalgae such as diatoms (*Navicula atomus* and *Diadesmis gallica*) have the ability to synthesize gold nanoparticles, gold, and silica-gold bionanocomposites (Mubarakali *et al*., 2013).

An important aspect of nanobiotechnology is to design economical and ecofriendly technique for the synthesis of nanomaterials and advancing the use of nanotechnology based materials in different applications. Although several chemical and physical methods are reported for the preparation of various metal nanoparticles, but they produce numerous non-biodegrable and hazardous by products, which are harmful to the environment (Kumar *et al*., 2016). However, for a biological process to successfully compete with chemical and physical nanostructure synthesis, strict control over average particle size in a specific size range and uniform particle morphology is required (Quester *et al*., 2013). Gold nanoparticles are highly demanded for different applications in various fields due to its low toxicity. Biosynthesis of gold nanoparticles (AuNPs) using bacteria (Kalishwaralal *et al*., 2009), fungi (Das *et al*., 2010), enzymes (Rangnekar *et al*., 2007), biomolecules (Rodriguez *et al*., 2014) and plant materials, including flower (Kumar *et al*., 2016), fruit (Kumar *et al*., 2016), leaf (Tahir *et al*., 2015), seed (Jayaseelan *et al*., 2013), oil (Kumar *et al*., 2016), etc., have become an attractive ecofriendly alternative option as compared to the chemical and physical methods.

Synthesis of Gold nanoparticles

Algae is considered as an important source of carbohydrates, protein and lipids. Interestingly, there are some noteworthy studies are reported in the literature for the synthesis of AuNPs using algae including *Fucus vesiculosus* (Mata *et al.*,2009), *Tetraselmis kochinensis* (Senapati *et al*., 2012), *Padina gymnospora* (Singh *et al*., 2013), *Sargassum muticum* (Lodeiro *et al*., 2013), *Turbinaria conoides* (Rajeshkumar *et al*., 2013), *Chlorella vulgaris* (Luangpipat *et al*., 2011), etc. Oza *et al*. (2012) studied the capability of biosynthesizing gold nanoparticles from gold salt solution under the influence of nitrate reductase in *Sargassum wightii* extract. The optimum conditions for biosynthesis of stable gold nanoparticles were alkaline pH and room temperature. The activity of nitrate reductase supports the view that they are involved in reducing and stabilizing the gold ions to gold nanoparticles. It presents a controllable method of tuning the synthesis of thermodynamically stable desired size and shape of gold nanoparticle. Oza *et al*. (2012) also reported that the *Chlorella pyrenoidusa* can be used for rapid synthesis of AuNPs.

Synthesis of nanogold has also been reported in algae, including *Chlorella vulgaris* (Ting *et al*., 1995), *Sargassum wightii* (Singaravelu *et al*., 2007) and *Plectonema boryanum* (Lengke *et al*., 2006a, 2006b). Gold nanoparticle synthesis of cyanobacteria (such as *Lyngbya majuscula* and *Spirulina subsalsa*), green algae (*Rhizoclonium hieroglyphicum* and *R. riparium*) and diatoms (*Nitzschia obtusa* and *Navicula minima*) has recently been reported by Chakraborty *et al*. (2006, 2009) and Nayak *et al*. (2006). Parial *et al*. (2012) demonstrated a green chemical approach for the controlled biosynthesis of gold nanorods by *Nostoc ellipsosporum* without any shape anisotropy. Kumar *et al*. (2016) showed the combination of *Calothrix algae* with ultrasound irradiation for the rapid synthesis of truncated shape AuNPs (30-120nm), which shows the presence of gold. This NPs act as a catalyst to convert to 4-NP to 4AP.

Seaweeds has been used to synthesize highly stable gold nanoparticles extracellularly. Extracellular synthesis of gold nanoparticles by *Sargassum wightii* a marine alga and red alga *Gracilaria corticata* has been reported by (Watson *et al*., 1999). Castro *et al*. (2013) concluded, that the size and shape of gold nanoparticle could be directly controlled by the initial pH value of the solution, especially in case of the red seaweed *Chondrus crispus*. In addition, the biosynthesis of gold and silver nanoparticles was also attained with the green alga *Spirogyra insignis* under the optimal conditions of synthesis including the possibility of metal recovery by absorption on the biomass surface.

The dried alga *Chlorella vulgaris*, a single- celled green alga, was found to have strong binding ability towards tetrachloroaurate ions to form algal-bound gold, which was subsequently reduced to Au (0). About, 90% of algal bound gold attained metallic state and the crystals of gold were accumulated in the inner and outer parts of cell surfaces with tetrahedral, decahedral and isohedral structures (Luangpipat *et al*., 2011). Parial *et al*. (2012) reported the green alga *Rhizoglonium fontinale* and *Ulva intestinalis* produced gold nanoparticles intracellularly, confirmed by purple colouration of the thallus within 72h of treatment at 20^0C. Extracted nanoparticles solutions were examined by UV-Vis Spectroscopy, transmission electron microscopy (TEM) and X-ray diffractometry (XRD). Naveena and Prakash (2013), reported the extracellular biosynthesis of gold nanoparticles from the marine algae *Gracilaria corticata* for its antimicrobial and antioxidant activity. It possess several biomedical properties such as antibacterial, antiviral, antifungal, antiprotozoal, anti-inflammatory, antioxidant, cytotoxic, contraception, gastrointestinal, cardiovascular, hypoglycaemia, antienzymes, spasmolytic and allelophatic effects (Hatano *et al*., 1988). Geetha *et al*. (2014) reported the intracellular synthesis of gold nanoparticles using marine cyanobacteria *Gloeocapsa* sp. for its antitumour activity on human cerival cancer cell line.

Synthesis and application of Silver nanoparticles

An aqueous solution of silver ions was treated with a live biomass of *Spirulina platensis* for the formation of crystallized silver nanoparticles (Mahdieh *et al*., 2012). Govindaraju *et al*. (2008) used *Spirulina platensis*, an edible blue green alga for the extracellular synthesis of gold, silver and Au/Ag bimetallic nanoparticles. Extracellular synthesis using aqueous extract of *Spirulina platensis* showed the formation of well scattered, highly stable, spherical AgNPs with an average size of 30-50nm (Sharma 2015). Ahmed *et al*. (2015) used environmental friendly method using *Spirulina platensis* and *Nostoc* sp. to synthesize AgNPs.

Rajeshkumar *et al*. (2012) documented synthesizing silver nanoparticles using low cost marine brown seaweed *Turbinaria conoides* as a reducing mediator. Salari *et al*. (2014) reported silver nanoparticles were synthesized through bio-reduction of silver ions using the *Spirogyra varians*. Some important studies on the production of silver nanoparticles by using marine algae *Chaetomorpha linum* and *Chaetoceros salina* by (Kannan *et al*., 2013 and Merin *et al*., 2010). Singaravelu *et al*. (2007), Rajasulochana *et al*. (2010) and Vivek *et al*.(2011), explored the synthesis of extracellular metal bionanoparticles using *Sargassum wightti*, *Kappaphycus alvarezii* and *Gelidiella acerosa*. Jena *et al*. (2012) found that the microalga *Chlorococcum humicola* has a high efficiency for synthesis of intracellular and extracellular AgNPs and its may become a great resource for nanoparticle formation.

Green microalgae and diatom could be employed for the green synthesis of nanoparticles was also suggested that the algal biomass can be produced using wastewater in order to treat various wastewaters. Karthikeyan *et al*. (2015) investigated the extracts of green microalgae, *Chlorella vulgaris* and the diatoms *Chaetoceros calcitrans* for synthesis of AgNPs.

The seaweeds are used (*Sargassum plagiophyllum*, *Ulva reticulata* and *Enteromorpha compressa*) for the synthesis of silver nanoparticles are widely recognised (Sudha *et al*., 2013). Microalgae have been shown to produce nanoparticles not only of silver but also of other metal ions such as gold, cadmium and platinum (Brayner *et al*., 2007 and Parial *et al*., 2012). Devinamerin *et al*. (2010) showed rapid synthesis of silver nanoparticles from the marine algae with high efficacy of antibacterial activity against human pathogens including *Escherichia coli*, *Klebsiella* sp, *Proteus vulgaris* and *Pseudomonas aeruginosa*. Intracellular or extracellular production of green synthesis nanoparticles generally depends on several factors such as microbial growth temperature, synthesis time, extraction methods and production ratio of sample (Nikolaos and Louise, 2014).

The AgNPs showed potential antimicrobial activity against human pathogens like *Staphylococcus aureus*, *Staphylococcus epidedymis*, *Klebsiella pneumonia*, *Escherichia coli* and *Pseudomonas aeruginosa*. Sudha *et al*. (2013) studied mangrove vegetation microalgae, in which *Microcoleus* sp. synthesized silver nanoparticles, showed an excellent antimicrobial activity. Silver nanoparticle have added a new dimension in the field of medicine concerning wound dressing and artificial implantation and in preventing contamination caused by microbes (Alaqad *et al*., 2016).

Application of algal-synthesized NPs

The biomedical application of algal-synthesized NPs is significantly becoming more important due to their antibacterial, antifungal, anticancer, and wound healing activity. Brown alga (*Bifurcaria bifurcata*) is reported for the synthesis of copper oxide nanoparticle exhibiting antibacterial activity against *Enterobactor aerogenes* (Gram negative) and *Staphylococcus aureus* (Gram positive) (Abboud *et al*., 2014). Synthesis of AgNPs using the aqueous extract of red seaweed *Gelidiella acerosa* as the reducing agent exhibited antifungal property against *Humicola insolens* (MTCC 4520), *Fusarium dimerum* (MTCC 6583), *Mucor indicus* (MTCC 3318) and *Tricoderma reesei* (MTCC 3929) (Marimuthu *et al*., 2011). Boca *et al*. (2011) synthesized chitosan-coated silver nano-triangles (chit-AgNPs) were used as a photothermal agents against a line of human lung cancer cells (NCI-H460). Govendaraju *et al*. (2015) synthesized the AgNPs using *Sargassum vulgare* and its ability to kill cancerous human myeloblastic leukemic cells HL60 and cervical cancer cells HeLa was tested. AuNPs has been proved as an important tool for hormone detection in pregnant women urine sample (Kuppusamy *et al*., 2014).

Conclusion

The use of algae in the synthesis of NPs has encouraged the designing of simple, green, cost and time effective approaches thereby, minimizing the use of chemicals and solvents. The developing era of nanoscience is a renowned gift for the development of science all over the world. Numerous studies conducted over the last decade, there are still considerable gaps in our knowledge about the biotechnological potential of green- synthesized nanoparticles. Improvements in the way that green synthesized nanoparticles are incorporated into medical devices could increase their efficacy and diminish any side effects. Owing to the diverse chemical ecology of algae, considerable research effort is still required to perfect this technology.

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