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Potential of Marine Macroalgae in Stabilizing Bio-Fabricated Nanoparticles for Photodegradation Application: A Review

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Abstrak

Makro alga laut, atau rumput laut, telah muncul sebagai sumber yang menjanjikan untuk sintesis hijau dan stabilisasi nano partikel, menawarkan potensi luar biasa dalam proses fotodegradasi. Sumber daya yang melimpah dan terbarukan ini menampung beragam senyawa bioaktif, termasuk polisakarida, protein, flavonoid, dan pigmen, yang dapat bertindak sebagai agen pereduksi dan penstabil. Integrasi agen stabilisasi yang diturunkan dari makroalga ke dalam sintesis nanopartikel memberikan sifat unik, meningkatkan kinerja dan stabilitas fotokatalitik. Ulasan ini secara komprehensif meneliti peran makroalga laut sebagai agen penstabil untuk bio-fabrikasi nanopartikel dalam aplikasi fotodegradasi khususnya untuk degradasi pewarna azo beracun dan senyawa organik. Ini mengeksplorasi ke dalam mekanisme sintesis nanopartikel dan stabilisasi, mengeksplorasi beragam spesies makroalga yang digunakan, dan mengevaluasi efisiensi fotokatalitik mereka terhadap berbagai polutan organik dan anorganik dalam air limbah. Selanjutnya, tinjauan ini secara kritis menganalisis tantangan dan perspektif masa depan di bidang ini, menawarkan wawasan tentang pengembangan strategi remediasi hijau, berkelanjutan, dan efisien untuk kontaminan lingkungan.

Kata kunci: Fotodegradasi, Fotokatalisis, Makroalga laut, Nanopartikel biogenik, Remediasi lingkungan

Abstract

Marine macroalgae, or seaweeds, have emerged as promising sources for the green synthesis and stabilization of nanoparticles, offering remarkable potential in photodegradation processes. These abundant and renewable resources harbor a diverse array of bioactive compounds, including polysaccharides, proteins, flavonoid, and pigments, which can act as reducing, capping, and stabilizing agents. The integration of macroalgae-derived stabilizing agents into nanoparticle synthesis confers unique properties, enhancing photocatalytic performance and stability. This review comprehensively examines the role of marine macroalgae as stabilizing agents for bio-fabricated nanoparticles in photodegradation applications in particular for toxic azo dye degradation and organic compounds. It explores into the mechanisms of nanoparticle synthesis and stabilization, explores the diverse macroalgal species employed, and evaluates their photocatalytic efficiency against various organic and inorganic pollutants in wastewater. Furthermore, the review critically analyzes the challenges and future

perspectives in this field, offering insights into the development of green, sustainable, and efficient remediation strategies for environmental contaminants.
Keywords: *Biogenic nanoparticles, Environmental remediation, Marine macroalgae, Photocatalysis, Photodegradation*

INTRODUCTION

The accelerated pace of industrialization and urbanization over the past few decades, a phenomenon documented extensively in numerous environmental scientist studies, has resulted in a significant escalation in the discharge of diverse pollutants into the environment, a trend that poses substantial challenges to environmental remediation efforts. These contaminants, ranging from organic dyes and pesticides to heavy metals and pharmaceuticals, pose severe threats to both ecological systems and human health. The pervasive nature of these pollutants necessitates the development of robust and sustainable remediation strategies to mitigate their deleterious ecological impacts. Within this context, photodegradation presents itself as a highly promising advanced oxidation process for the effective treatment of a wide spectrum of persistent organic pollutants found in wastewater, including but not limited to toxic azo dyes and recalcitrant organic (Bhanderi et al., 2024).

Photodegradation, more precisely termed photocatalytic degradation, is an advanced oxidation process that leverages photonic energy to catalyze chemical reactions, thereby initiating the decomposition of a wide array of environmental contaminants, encompassing both organic and inorganic pollutants (Mohammed et al., 2023; Qutub et al., 2022). This technology has garnered substantial interest within the scientific community due to its inherent potential for complete mineralization of pollutants, low operational costs, and the ability to utilize renewable solar energy (Shi et al., 2023). However, it is crucial to acknowledge that the efficacy of photodegradation is fundamentally contingent upon the performance characteristics of the employed photocatalyst. Conventional photocatalytic materials, while demonstrating promise, often exhibit inherent limitations, including but not limited to issues of long-term stability, insufficient active surface area, and the rapid recombination of photogenerated electron-hole pairs (Rahman et al., 2022).

These limitations underscore the need for enhance the photocatalytic performance and overcome the limitations of conventional photocatalysts, researchers have explored the use of various stabilizing agents. These stabilizers play a crucial role in preventing agglomeration, improving dispersion, and enhancing the overall stability of the photocatalysts (Heuer-Jungemann et al., 2019; Munnik et al., 2015). In the ongoing search for effective solutions to these limitations, bio-fabricated nanoparticles derived from marine macroalgae have emerged as a particularly compelling area of research. This interest, evidenced by the growing body of literature on the topic, stems from the unique physicochemical properties of these biogenic nanoparticles, their inherently eco-friendly nature, and their promising potential for sustainable large-scale production (Abuzeid et al., 2023; Österberg et al., 2023).

Marine macroalgae, colloquially termed seaweeds, represent a vast and diverse group of eukaryotic photosynthetic organisms inhabiting a wide range of marine environments. Notably, these organisms are rich in a diverse array of bioactive compounds, including but not limited to polysaccharides, proteins, and pigments. This rich biochemical diversity renders them exceptionally well-suited for serving as stabilizing agents in nanoparticle synthesis. The utilization of marine macroalgae in this domain offers several key advantages that surpass conventional methods. These advantages include their nature as renewable and readily available resources, their inherent biocompatibility, and their capacity to facilitate the green synthesis of nanoparticles – aligning with the core principles of sustainable chemistry (Wen et al., 2024).

This comprehensive review endeavors to provide an in-depth examination of the multifaceted role of marine macroalgae as stabilizing agents for bio-fabricated nanoparticles in photodegradation processes. It will explore the various species of macroalgae employed, the mechanisms of nanoparticle synthesis and stabilization, and the photocatalytic performance of these bio-fabricated nanoparticles for the degradation of different pollutants. Additionally, the review will highlight the challenges and future perspectives in this field, contributing to the development of sustainable and efficient remediation strategies for environmental pollutants.

Marine Macroalgae as a Source of Bio-fabricated Nanoparticles

Marine macroalgae, more commonly referred to as seaweeds, comprise a vast and diverse group of multicellular, eukaryotic organisms. These macroalgae inhabit a wide array of aquatic ecosystems, spanning from the open ocean to shallower coastal regions and intertidal zones (Leandro et al., 2020). Taxonomically, these macroalgae are broadly categorized into three primary phyla: Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae) (Jimenez-Lopez et al., 2021). Each group possesses a unique array of biochemical constituents that contribute to their potential for nanoparticle synthesis.

Within this diverse assemblage, the genus *Sargassum*, a member of the phylum Phaeophyta (brown algae), has garnered significant attention due to its exceptional richness in a wide array of bioactive compounds. These compounds encompass, but are not limited to, polyphenols, polysaccharides, phytohormones, carotenoids, vitamins, unsaturated fatty acids, and free amino acids (Rushdi et al., 2020). These diverse metabolites exhibit remarkable properties that are highly advantageous in the context of nanomaterial synthesis. Specifically, they possess potent reducing capabilities, can effectively cap growing nanoparticles, and impart long-term stability – attributes that make them exceptionally well-suited for the biosynthesis of metallic nanoparticles. This includes, but is not limited to, the synthesis of noble metal nanoparticles such as silver (Ag) and gold (Au), as well as metal oxide nanoparticles such as zinc oxide (ZnO) and iron oxide (Fe_3O_4) (Marslin et al., 2018).

Figure 1. The marine seaweed, *Lobophora variegata* which was used for catalytic activity agains organic pollutants of nitrophenol (adopted and modified from El-Beltagi et al., (2022) is licensed under CC BY 4.0).

Beyond *Sargassum*, other marine macroalgae have also demonstrated significant potential in the realm of biogenic nanoparticle synthesis. For instance, the species *Padina tetrastromatica*, belonging to the phylum Phaeophyta, harbors a diverse repertoire of biomolecules, including flavonoids, steroids, saponins, tannins, phenols, and proteins. These compounds, much like those found in *Sargassum*, can act as effective reducing, capping, and stabilizing agents during nanoparticle synthesis (Princy & Gopinath, 2018). This remarkable diversity of biomolecules present within various species of marine macroalgae offers a vast and largely untapped reservoir of resources for the sustainable bio-fabrication of nanoparticles. This approach holds significant promise for tailoring nanoparticles with specific properties and functionalities, thereby expanding their potential applications in fields such as environmental remediation.

Table 1. Characteristics of marine macroalgae used as stabilizing agents for bio-fabricated nanoparticles.

Species of Macroalgal	Bioactive Substances	Phytochemical Activities	NPs synthesized and produced	Size of NPs (nm)	Shape of NPs	Reference
Padina sp.	Polyphenol, cyclononasiloxane, octadecamethyl, hexadecanoic acid, fatty acid	Reducing and capping agents	Ag	40.45	Polydispersed spherical and oval-shaped	(Bhuyar et al., 2020)
Sargassum polycystum	Phenolic and flavonoids	Reducing and stabilizing agent	Ag	<100	Spherical	(Thiurunavukkarau et al., 2022)
Colpomenia sinuosa	Proteins, phenols, sulphated polysaccharide	Reducing and stabilizing agent	Ag	<40	Spherical	(Ghareeb et al., 2022)
Corallina mediterranea	Proteins, phenols, sulphated polysaccharide	Reducing and stabilizing agent	Ag	<40	Spherical	(Ghareeb et al., 2022)
Ulva rigida	Terpenoids, polyphenols, carotenoids, fatty acids, carbohydrates, and lipids	Reducing and capping agents	Ag	12.6	Spherical	(Algotiml et al., 2022)
Cystoseira myrica	Polyphenols, sulfonated	Reducing and	Ag	17	Spherical	(Algotiml et al., 2022)

Species of Macroalgal	**Bioactive Substances**	**Phytochemical Activities**	**NPs synthesized and produced**	**Size of NPs (nm)**	**Shape of NPs**	**Reference**
	polysaccharides (fucoidan), sterols, and lipids	capping agents				
Gracilaria foliifera	Agar and sulfonated polysaccharides	Reducing and capping agents	Ag	24.5	Spherical	(Algotiml et al., 2022)

Marine macroalgae represent a rich repository of bioactive compounds, encompassing a wide spectrum of molecules such as polyphenols, polysaccharides, proteins, and an array of secondary metabolites as shown in **Table 1**. This remarkable biochemical diversity confers upon these organisms the capacity to effectively reduce metal ions, facilitating the nucleation and growth of nanoparticles. Moreover, these biomolecules can effectively stabilize the resultant nanoparticles, preventing aggregation and enhancing their long-term stability. Nanoparticles synthesized via this environmentally benign, biologically-mediated approach, employing extracts derived from marine macroalgae, are typically referred to as bio-fabricated or biogenic nanomaterials.

For instance, species within the genus *Padina*, such as *Padina pavonica,* are known to harbor a diverse array of biomolecules, including polyphenols, cyclononasiloxane, octadecamethyl, hexadecanoic acid, and various other fatty acids. These compounds have been shown to function effectively as both reducing and capping agents during the synthesis of silver nanoparticles (AgNPs). Characterization of the resultant biogenic AgNPs revealed an average particle size of 40.45 nm, with a morphology characterized by a polydispersed distribution of spherical and oval-shaped particles (Bhuyar et al., 2020). Similarly, extracts derived from the brown alga *Sargassum polycystum,* rich in phenolic compounds and flavonoids, have been successfully employed in the biosynthesis of AgNPs. These biogenic nanoparticles exhibited sizes primarily below 100 nm and displayed a predominantly spherical morphology, highlighting the role of the algal biomolecules in controlling nanoparticle growth and morphology (Thiurunavukkarau et al., 2022).

Furthermore, studies utilizing extracts from *Colpomenia sinuosa* and *Corallina mediterranea*, species belonging to the Phaeophyceae and Rhodophyta respectively, have also demonstrated the successful biosynthesis of AgNPs. The presence of proteins, phenols, and sulfated polysaccharides in these algal extracts contributes to their efficacy as reducing and stabilizing agents during nanoparticle formation. In these instances, the resulting AgNPs exhibited sizes predominantly below 40 nm and displayed a consistent spherical morphology. These findings further underscore the diversity of macroalgal species and their bioactive constituents that can be leveraged for the tailored synthesis of metallic nanoparticles (Ghareeb et al., 2022). *Ulva rigida*, a green macroalga belonging to the Chlorophyta, presents yet another compelling example. This species, rich in terpenoids, polyphenols, carotenoids, fatty acids, carbohydrates, and lipids, has been successfully employed for the biosynthesis of AgNPs. The diverse array of biomolecules in *Ulva rigida* extracts acts synergistically, serving as both reducing and capping agents during nanoparticle formation. This process yields spherical AgNPs with an average size of 12.6 nm, highlighting the capacity for precise size control using this particular macroalgal species (Algotiml et al., 2022).

Cystoseira myrica, another representative of the Phaeophyceae, further exemplifies the potential of brown algae in biogenic nanoparticle synthesis. This species, characterized by a high content of polyphenols, sulfated polysaccharides (including fucoidan), sterols, and lipids, has been demonstrated to facilitate the production of AgNPs with well-defined characteristics. Specifically, these biomolecules act synergistically as reducing and capping agents, yielding spherical AgNPs with an average size of 17 nm. The consistent size and morphology of the biosynthesized nanoparticles underscore the significant role of the *Cystoseira myrica* biomolecular profile in controlling nanoparticle nucleation and growth (Algotiml et al., 2022). Turning to the Rhodophyta, *Gracilaria foliifera*, a commercially valuable red alga, offers yet another distinct biochemical profile for biogenic nanoparticle synthesis. This species is particularly notable for its high agar content, in addition to other sulfated polysaccharides. These polysaccharides act effectively as reducing and capping agents during the formation of AgNPs. The resultant biogenic AgNPs, characterized by a spherical morphology, exhibit an average size of 24.5 nm, further demonstrating the capacity for size control through the selection of macroalgal species with tailored biomolecular profiles (Algotiml et al., 2022).

As comprehensively illustrated in Table 1, marine macroalgae exhibit a remarkable diversity in their chemical composition. This includes a rich repertoire of bioactive compounds, encompassing polyphenols, polysaccharides (including agar, carrageenan, and fucoidan), proteins, and an array of other secondary metabolites. It is this very diversity that underpins the efficacy of macroalgae as both reducing and stabilizing agents in the biosynthesis of metal nanoparticles, with silver nanoparticles (AgNPs) being a prominent example. Importantly, the size, shape, and physicochemical properties of the resultant nanoparticles are influenced by a confluence of factors, most notably the specific macroalgal species employed and the nuanced parameters of the biosynthesis methods utilized.

Numerous methods have been explored for the biosynthesis of nanoparticles utilizing marine macroalgae as sustainable and versatile bio-factories. These methods leverage the inherent reducing, capping, and stabilizing properties of the diverse biomolecules present within these organisms. A common and highly effective approach involves the initial extraction of bioactive compounds from the algal biomass. This is typically achieved using aqueous or solvent-based extraction techniques, optimized for the targeted biomolecules. The extracted biomolecules are then reacted with metal salts or precursors under carefully controlled conditions, including parameters such as temperature, pH, and reaction time. Precise control over these reaction parameters is crucial for directing nanoparticle nucleation, growth, and ultimately, the desired physicochemical properties of the biogenic nanoparticles (Mukherjee et al., 2021).

For instance, in a study by Karkhane et al. , *Sargassum vulgare* extract was successfully employed for the biosynthesis of zinc oxide (ZnO) nanoparticles. This eco-friendly synthesis approach yielded spherical ZnO nanoparticles with sizes ranging from 50 to 150 nm. The study highlighted the dual role of the *Sargassum vulgare* extract, functioning both as a reducing agent, facilitating the conversion of metal ions to their zero-valent state, and as a capping agent, controlling nanoparticle growth and preventing aggregation. This example underscores the potential of harnessing macroalgal biodiversity for the green synthesis of diverse metal oxide nanoparticles (Karkhane et al., 2020). Similarly, Balaraman et al. demonstrated the successful biosynthesis of silver (Ag) nanoparticles using extracts derived from *Sargassum myriocystum*. In this instance, the phenolic compounds, abundant in the Sargassum extract, played a pivotal role as both reducing and capping agents, driving nanoparticle formation and stabilization. This biogenic approach yielded well-dispersed Ag nanoparticles exhibiting a hexagonal morphology and an average size of 20 ± 2.2 nm, further highlighting the capacity for shape control using macroalgal-mediated synthesis (Balaraman et al., 2020).

It is noteworthy that biosynthesis of nanoparticles using macroalgae is not always contingent upon the initial extraction of bioactive compounds. In certain instances, the process can be effectively carried out using the intact algal biomass itself. One such example involves the use of *Sargassum coreanum* for the green synthesis of silver nanoparticles. In this particular approach, the polysaccharides, polyphenols, and lignans inherently present in the *Sargassum* biomass act synergistically as reducing and stabilizing agents, obviating the need for separate extraction steps. This method yielded distorted spherical silver nanoparticles with an average size of 19 nm, demonstrating the feasibility of direct biomass utilization for nanoparticle biosynthesis (Somasundaram et al., 2021).

The utilization of marine macroalgae as a source of renewable and inherently sustainable bioresources for nanoparticle biosynthesis presents a compelling and increasingly viable alternative to conventional physicochemical synthesis methods. This burgeoning field of research is driven by the numerous advantages offered by macroalgae, which align with the core principles of green chemistry and sustainable nanotechnology. First and foremost, these macroalgae represent an abundant and, crucially, renewable resource for nanoparticle production, addressing a key sustainability concern associated with conventional synthesis methods that often rely on finite and potentially toxic precursors. Moreover, the biogenic nanoparticles synthesized using macroalgal extracts inherently benefit from the biocompatible and generally low-toxicity nature of these biological materials. This is largely attributed to the fact that the nanoparticles are often inherently coated or capped by the bioactive compounds derived from the algal extracts, such as polysaccharides and proteins. This natural coating can mitigate potential adverse effects on human health and minimize ecological risks, factors of paramount concern in the development of sustainable nanomaterials. Moreover, the remarkable diversity of biomolecules presents in marine macroalgae, including polyphenols, polysaccharides, proteins, and various other metabolites, endows them with remarkable reducing, capping, and stabilizing capabilities, enabling the synthesis of a wide array of nanoparticles with unique properties and functionalities.

Furthermore, the inherent tunability of biosynthesis using macroalgae represents a significant advantage. Researchers can exert control over several critical parameters during the synthesis process, thereby tailoring the properties of the resulting nanoparticles with a high degree of precision. These parameters include, but are not limited to, the concentration of the algal extract employed, reaction temperature, pH, and reaction time. By systematically adjusting these variables, it becomes possible to direct nanoparticle size, shape, and even morphology, influencing their downstream applications. From an economic standpoint, the utilization of these abundant algal resources significantly reduces production costs compared to conventional chemical and physical methods, rendering the process more economically viable. A particularly compelling aspect of macroalgae-mediated biosynthesis is that the resulting nanoparticles often exhibit multifunctional properties. This can be directly attributed to the presence of bioactive molecules from the algal extracts, which effectively functionalize the nanoparticle surfaces. The synergistic effects of these biomolecules can impart a range of desirable properties to the nanoparticles, including enhanced antimicrobial activity, potent antioxidant capacity, and often, exceptional catalytic activity. This inherent multifunctionality significantly broadens the potential applications of these biogenic nanoparticles, extending their utility across diverse fields such as biomedicine, environmental remediation, and industrial catalysis, among others.

Role of Marine Macroalgae as Stabilizing Agents

Nanoparticle stabilization refers to the process of preventing nanoparticles from agglomerating or aggregating, thereby maintaining their dispersed state and unique properties (Laurent et al., 2008). This inherent stability conferred by the biogenic capping agents is of paramount importance in numerous technological applications, particularly in the realm of photodegradation processes. In such processes, nanoparticles, especially metal and metal oxide nanoparticles, are frequently employed as photocatalysts or photosensitizers. Their role is to effectively facilitate the breakdown of recalcitrant organic pollutants or contaminants upon exposure to light irradiation. However, a key challenge in this domain is the often-observed aggregation of nanoparticles, which significantly diminishes their photocatalytic efficiency. This is where the stabilizing role of the biomolecules derived from macroalgae becomes particularly critical. Hence, a critical challenge in leveraging nanoparticles for photodegradation lies in their inherent tendency to agglomerate. This agglomeration stems from the high surface energy and reactive nature of nanoparticles, particularly those in the nanoscale regime. As nanoparticles aggregate, their effective surface area available for catalytic activity diminishes, thereby reducing their overall efficiency in photodegradation processes (Pellegrino et al., 2017). Stabilization techniques are employed to counteract these tendencies and maintain the nanoparticles' high surface area and reactivity (Khan et al., 2022).

Marine macroalgae employ a variety of mechanisms to effectively stabilize nanoparticles, preventing their agglomeration and maintaining their dispersed state and unique properties (Sidhu et al., 2022). One prominent mechanism is electrostatic stabilization, where charged biomolecules like polysaccharides or proteins present in the macroalgae electrostatically interact with the nanoparticle surface, creating repulsive forces that inhibit agglomeration (Matter et al., 2020; Österberg et al., 2023). Steric stabilization is another crucial mechanism, facilitated by the adsorption of long-chain polymers or macromolecules from the macroalgae onto the nanoparticle surface, forming a physical barrier that hinders close contact and aggregation (Bajpai et al., 2007). Additionally, certain marine macroalgae possess functional groups capable of forming complexes or chelating with metal ions in nanoparticles, leading to stabilization through strong coordination bonds (Iddrisu et al., 2024). Furthermore, the antioxidant properties of many marine macroalgae, attributed to their polyphenol, carotenoid, and other bioactive compound content, play a role in scavenging reactive oxygen species and preventing nanoparticle oxidation, thereby enhancing stability (Lomartire & Gonçalves, 2023). The remarkable diversity of chemical structures found within marine macroalgae provides an elegant solution to this challenge. Polysaccharides such as alginates and carrageenans, proteins, lipids, and an array of other bioactive compounds, each with their unique structural features, can effectively interact with nanoparticle surfaces, providing steric hindrance, electrostatic repulsion, or both, and thereby preventing agglomeration. These multifaceted stabilization mechanisms, conferred by the inherent chemical richness of marine macroalgae, position them as highly effective and versatile stabilizing agents for nanoparticles, particularly in applications where maintaining high surface area and reactivity is paramount, such as photodegradation (Ahmad et al., 2022).

The utilization of marine macroalgae as stabilizers for nanoparticles offers several compelling advantages over conventional synthetic stabilizers. Firstly, marine macroalgae are natural, renewable, and biodegradable resources, rendering them environmentally friendly and biocompatible, in contrast to synthetic stabilizers that may pose potential toxicity concerns. Additionally, the abundance and accessibility of marine macroalgae make them a cost-effective alternative to expensive synthetic stabilizers. Notably, these marine organisms possess multifunctional properties, imparting not only stabilization but also additional functionalities to nanoparticles, such as antioxidant, antimicrobial, or therapeutic properties, depending on their bioactive composition. Furthermore, the diverse chemical composition of marine macroalgae allows for the tailored selection of specific species or combinations to customize the stabilization mechanism and properties of nanoparticles for specific applications. Remarkably, the combination of marine macroalgae with nanoparticles can lead to synergistic effects, enhancing their overall performance in various applications, including photodegradation processes. By leveraging these advantages, researchers and industry can develop more sustainable, cost-effective, and environmentally friendly nanoparticle-based systems, while also benefiting from the unique properties and stabilization mechanisms provided by marine macroalgae.

Table 2. Physicochemical properties of bio-fabricated nanoparticles stabilized by marine macroalgae.

Species of Macroalgal	Bioactive Substances	NPs synthesized and produced	Particle Size	Zeta Potential	Surface Area (m^2/g)	Reference
Padina boryana	Phenols, aliphatic hydrocarbons, aromatic rings, and aliphatic amine	Pd	5-20 nm	− 28.7 ± 1.6 mV	16.1	(Sonbol et al., 2021)
Ulva lactuca	Phenols, carbonyl compounds, carboxylic acids, amines, polysaccharides, polyphenols, and	Ag	5-40 nm	−59.0 mV	NR*	(Maduraimuthu et al., 2023)

Species of Macroalgal	Bioactive Substances	NPs synthesized and produced	Particle Size	Zeta Potential	Surface Area (m^2/g)	Reference
	proteins					
Sargassum spp.	Ase terpenoids, flavones, and polysaccharides	Fe_3O_4	23.60 ± 0.62 nm	NR*	45.11	(Bhole et al., 2023)

*NR: Not Reported

The physicochemical properties of bio-fabricated nanoparticles stabilized by marine macroalgae are crucial in understanding their potential applications and behavior in various environments. The investigations as shown in **Table 2** will provide a comprehensive and cohesive discussion of the relevant physicochemical properties, such as particle size, zeta potential, and surface area, for selected species of macroalgae.

The successful utilization of *Padina boryana*, a brown macroalga, for the biosynthesis of palladium nanoparticles (Pd NPs) exemplifies the points discussed above. The rich repertoire of bioactive substances presents in *P. boryana*, including phenols, aliphatic hydrocarbons, aromatic compounds, and aliphatic amines, plays a crucial multifaceted role in both the reduction of palladium ions and the subsequent stabilization of the formed nanoparticles. Characterization of the biogenic Pd NPs revealed a particle size distribution in the range of 5–20 nm. Importantly, these nanoparticles exhibited a zeta potential of −28.7 ± 1.6 mV, a value indicative of moderate electrostatic stabilization, further highlighting the role of the algal biomolecules in preventing nanoparticle aggregation. Moreover, the synthesized Pd NPs possessed a remarkably high surface area of 16.1 m^2/g, a highly desirable attribute for applications such as catalysis and sensing, where a large surface area directly correlates with enhanced performance (Sonbol et al., 2021).

The biosynthesis of silver nanoparticles (Ag NPs) using *Ulva lactuca*, a widely distributed green macroalga, provides another compelling example of the efficacy of this approach. *U. lactuca* is known for its rich and diverse profile of bioactive substances, encompassing phenols, carbonyl compounds, carboxylic acids, amines, polysaccharides, polyphenols, and proteins. This diverse array of biomolecules acts synergistically to both reduce silver ions and stabilize the nascent Ag NPs, preventing their aggregation and preserving their unique properties. Characterization of the biosynthesized Ag NPs revealed a particle size distribution ranging from 5 to 40 nm. Notably, these nanoparticles exhibited a zeta potential of −59.0 mV, a value indicative of excellent colloidal stability. This high negative zeta potential highlights the effectiveness of the U. lactuca biomolecules in imparting long-term stability to the nanoparticles, a crucial attribute for their application in various domains. However, the surface area of the synthesized Ag NPs has not been reported (NR) in the study by (Maduraimuthu et al., 2023).

Sargassum spp., a genus of brown macroalgae renowned for its rich diversity of bioactive compounds, has also emerged as a promising candidate for the green synthesis of iron oxide nanoparticles (Fe_3O_4 NPs). The presence of sesquiterpene terpenoids, flavones, and various polysaccharides within *Sargassum* spp. contributes significantly to their efficacy as both reducing and stabilizing agents during nanoparticle synthesis. For instance, a study by Bhole et al. demonstrated the synthesis of Fe_3O_4 NPs using *Sargassum* extracts, yielding nanoparticles with an average size of 23.60 ± 0.62 nm and a notably high surface area of 45.11 m^2/g. This high surface area is particularly advantageous for applications such as catalysis and adsorption, where a larger surface area translates to enhanced reactivity. However, it is important to note that the study did not report the zeta potential of the synthesized Fe_3O_4 NPs, a crucial parameter for assessing their colloidal stability and potential for agglomeration. Future investigations focused on characterizing the zeta potential of *Sargassum*-derived Fe_3O_4 NPs will be essential in fully elucidating their stability profiles and long-term performance characteristics (Bhole et al., 2023).

It is crucial to recognize that the physicochemical properties of bio-fabricated nanoparticles stabilized by marine macroalgae are intricately linked to the specific composition of bioactive substances present within the algal species employed. These properties, which include, but are not limited to, particle size, zeta potential, and surface area, exert a profound influence on the potential applications and overall behavior of the synthesized nanoparticles. For example, in applications such as catalysis, smaller particle sizes are generally preferred as they translate to a higher surface area-to-volume ratio, thereby increasing the number of active sites available for catalytic reactions. Similarly, a high surface area is desirable in applications such as adsorption and sensing, where a larger interfacial area enhances the interaction between the nanoparticles and target molecules. Zeta potential, a measure of the electrostatic potential at the nanoparticle surface, is a critical indicator of colloidal stability. A high zeta potential value, whether positive or negative, indicates a strong electrostatic repulsion between nanoparticles, which effectively prevents their aggregation and maintains their dispersion in solution. This colloidal stability is paramount in various applications, including drug delivery, where nanoparticles must remain stably dispersed in biological fluids to effectively deliver their payload, and biosensing, where nanoparticle aggregation can compromise the sensitivity and accuracy of detection. Therefore, the judicious selection of macroalgal species, with their unique repertoire of bioactive compounds, combined with precise control over synthesis parameters, allows for the tailored design of biogenic nanoparticles with optimized physicochemical properties for a wide range of applications.

The studies discussed herein, encompassing a diverse range of macroalgal species and nanoparticle compositions, provide compelling evidence for the immense potential of marine macroalgae as eco-friendly and economically viable bio-factories for nanoparticle synthesis. Their inherent capacity to act as both reducing and stabilizing agents, stemming from their rich diversity of bioactive constituents, positions them as highly attractive alternatives to conventional, often environmentally burdensome, synthesis methods. However, it is crucial to acknowledge that this field of research is still in its relative infancy. Further in-depth investigations are warranted to develop a more comprehensive and mechanistic understanding of the intricate interplay between the specific macroalgal species employed, their unique profile of bioactive molecules, and the resulting physicochemical properties of the synthesized nanoparticles.

Recent Advances in Marine Macroalgae-Stabilized Nanoparticles for Photodegradation

Recent research studies have unveiled the remarkable potential of marine macroalgae-stabilized nanoparticles for photodegradation of various pollutants as shown by **Table 3**. These nanoparticles synthesized using diverse macroalgae species such as brown seaweeds (e.g., *Sargassum*, *Padina*, *Turbinaria*), red seaweeds (e.g., *Gracilaria*), and green seaweeds (e.g., *Ulva*, *Caulerpa*), have demonstrated exceptional photocatalytic activity in degrading a wide range of organic and inorganic contaminants, including dyes, phenolic compounds, pesticides, and heavy metals. The synergistic effect of the nanoparticles' inherent photocatalytic properties and the macroalgae-derived stabilizing agents, often possessing antioxidant and redox capabilities, contributes to enhanced photodegradation efficiency. Moreover, the utilization of these eco-friendly, renewable, and cost-effective macroalgae resources as stabilizing agents aligns with the principles of green chemistry and sustainability, making these systems attractive for environmental remediation applications.

While the use of marine macroalgae-stabilized nanoparticles for photodegradation of pollutants holds great promise, several challenges and limitations must be addressed. Achieving consistent and large-scale production of these nanoparticles with uniform properties remains a challenge due to the variability in macroalgae composition and the complexity of the synthesis processes. Long-term stability of the nanoparticles in various environmental conditions and potential leaching of metal ions or other components are crucial factors that need thorough investigation to ensure their safe and effective application. Additionally, while the broad-spectrum photodegradation capabilities of these systems are advantageous, developing selective and specific systems for targeting particular pollutants or mixtures may be necessary in certain applications. Comprehensive toxicological studies are also required to assess the potential ecological and human health risks associated with the use of these nanoparticles, particularly in aquatic environments or when applied in large-scale remediation efforts. Furthermore, optimization of synthesis conditions, nanoparticle properties, and photodegradation processes, as well as integration of these systems into existing water treatment or environmental remediation technologies, require further research efforts.

Table 3. Photodegradation activity of bio-fabricated nanoparticles stabilized by marine macroalgae against target pollutants.

Species of Algae	Bioactive/Stabilizing agent	Reaction Time	Surface area (m^2/g)	Catalyst Dose	NPs synthesized and produced	Target Pollutants	Photodegradation efficiency (%)/degradation rate constant	Reference

Species of Algae	Bioactive/Stabilizing agent	Reaction Time	Surface area (m^2/g)	Catalyst Dose	NPs synthesized and produced	Target Pollutants	Photodegradation efficiency (%)/degradation rate constant	Reference
Ulva lactuca	Polyphenols, amino acids, vitamins, and enzymes	180 min	NR*	2.5	ZnO	Methyl red	90	(Anjali et al., 2022)
Stoechospermum marginatum	Polyphenols, amino acids, vitamins, and enzymes	180 min	NR*	2.5	ZnO	Methyl red	92	(Anjali et al., 2022)
Saragassum cervicorne	Protein molecules, alginates or sulphated polysaccharides and polyols	9 min	NR*	40 µg/µL	Pd	Congo red	99.25	(Anwar et al., 2021)
Saragassum cervicorne	Protein molecules, alginates or sulphated polysaccharides and polyols	10 min	NR*	60 µg/µL	Pd	Mehyl Orange	99.66	(Anwar et al., 2021)
Saragassum cervicorne	Protein molecules, alginates or sulphated polysaccharides and polyols	15 min	NR*	80 µg/µL	Pd	Methyl red	95.45	(Anwar et al., 2021)
Lobophora variegata	Alcohols, phenols, carboxylic acid, and carbonyl	4 min	NR*	1	Au	4-nitrophenol (4NP)	8.8×10^{-3} sec^{-1}	(Kaithavelikkakath Francis et al., 2020)
Lobophora variegata	Alcohols, phenols, carboxylic acid, and carbonyl	8 min	NR^*	1	Au	3-nitrophenol (4NP)	4.5×10^{-3} sec^{-1}	(Kaithavelikkakath Francis et al., 2020)

Species of Algae	Bioactive/Stabilizing agent	Reaction Time	Surface area (m^2/g)	Catalyst Dose	NPs synthesized and produced	Target Pollutants	Photodegradation efficiency (%)/degradation rate constant	Reference
Lobophora variegata	Alcohols, phenols, carboxylic acid, and carbonyl	3 min	NR*	1	Au	2-nitrophenol (4NP)	12.1×10^{-3} sec^{-1}	(Kaithavelikkakath Francis et al., 2020)

*NR: Not Reported

The photocatalytic degradation of persistent organic pollutants, a significant environmental concern, has emerged as a promising avenue for remediation. This approach leverages the unique photocatalytic properties of nanoparticles (NPs), particularly their ability to efficiently generate reactive oxygen species (ROS) upon exposure to light irradiation. In recent years, the scientific community has witnessed a surge of interest in utilizing marine macroalgae as a sustainable and environmentally benign source for both the synthesis and stabilization of these photocatalytically active NPs. These bio-fabricated NPs exhibit remarkable photodegradation potential against a wide range of target pollutants, offering a compelling solution for effective wastewater treatment and environmental decontamination.

The brown macroalga *Sargassum cervicorne*, known for its abundance and biochemical richness, has emerged as a particularly promising candidate for the biosynthesis and stabilization of photocatalytically active nanoparticles. For instance, Anwar et al. (2024) reported a facile and green method for the fabrication of copper nanoparticles (Cu NPs) employing alginates extracted from *S. cervicorne* as the stabilizing agent (Anwar et al., 2024). The resultant biogenic Cu NPs exhibited exceptional photocatalytic activity against a range of toxic azo dyes, including Methyl Orange (MO), Congo Red (CR), and Methyl Red (MR). The authors reported remarkable degradation efficiencies, ranging from 92.02% to 98.58%, highlighting the efficacy of this approach. The observed high surface area of the synthesized Cu NPs (4.03 m^2/g), coupled with the identification of an optimal catalyst dose (120–200 μg/mL), provides valuable insights into the factors governing their exceptional performance in photodegradation.

In a distinct approach, Koca et al. (2023) explored the use of *Desmarestia menziesii* extract, a brown alga, for the synthesis of hollow nanofibers (hNFs) with photocatalytic properties (Koca et al., 2023). These biogenic hNFs exhibited promising photodegradation activity against the model dyes Methylene Blue and Brilliant Blue. Specifically, they achieved a degradation efficiency of 69.81% for Methylene Blue and 75.7% for Brilliant Blue after a reaction time of 210 minutes, with a catalyst dose of 2 mg/L. This study highlights the potential of leveraging macroalgae not only for nanoparticle synthesis but also for generating more complex nanostructures with tailored photocatalytic properties.

Lavanya et al. (2023) focused their research on the green synthesis of silver nanoparticles (Ag NPs) using extracts from the green macroalga *Halimeda macroloba* (Lavanya et al., 2023). The authors attributed the successful reduction and stabilization of the Ag NPs to the rich repertoire of bioactive compounds in *H. macroloba* extract, including phenols, carbohydrates, tannins, and saponins. These biogenic Ag NPs exhibited impressive photocatalytic performance, degrading 91.35% of Methylene Blue within a reaction time of 100 minutes, using a catalyst dose of 10 mg/L. This study further exemplifies the capacity of diverse macroalgal species to drive the synthesis of photocatalytically active nanoparticles against harmful dyes.

Meky et al. (2023) investigated a novel approach, employing extracts from the red macroalga *Pterocladia capillacea* to synthesize cobalt-doped zinc oxide nanoparticles (Co-ZnO NPs) (Meky et al., 2023). The presence of proteins, peptides, carbohydrates, and pigments within the *P. capillacea* extract contributed to both the reduction of metal ions and the stabilization of the resulting Co-ZnO NPs. Notably, these biogenic nanoparticles exhibited exceptional photocatalytic activity against ciprofloxacin (CIPF), a widely used antibiotic and a contaminant of emerging concern. The authors reported an impressive degradation efficiency of 99.75% after only 45 minutes of reaction time, using a catalyst dose of 76.96 mg/L. The synthesized Co-ZnO NPs possessed a relatively high surface area of 15.114 m^2/g, which likely contributed to their enhanced photocatalytic performance. This study underscores the potential of leveraging macroalgae to synthesize doped metal oxide nanoparticles with tailored compositions and superior photocatalytic properties.

The remarkable photodegradation efficiencies exhibited by these bio-fabricated nanoparticles underscore the profound influence of the macroalgal extracts used in their synthesis. These extracts, rich in a diverse array of bioactive compounds, play a multifaceted role, acting as both reducing agents, facilitating the formation of nanoparticles from metal ions, and as stabilizing agents, preventing their aggregation and enhancing their long-term stability.

The presence of various bioactive compounds within the macroalgal extracts, including but not limited to polyphenols, amino acids, vitamins, enzymes, proteins, carbohydrates, and pigments, contributes synergistically to these desirable properties. For instance, polyphenols, known for their antioxidant and reducing capabilities, can effectively donate electrons to metal ions, reducing them to their zero-valent state and promoting nanoparticle nucleation. Simultaneously, these biomolecules can effectively adsorb onto the surface of the forming nanoparticles, creating a protective capping layer that prevents their uncontrolled growth and aggregation.

This natural capping layer not only enhances the stability of the nanoparticles, preventing their agglomeration and preserving their high surface area, but can also influence their photocatalytic performance through various mechanisms. These include enhancing light absorption, promoting efficient charge separation, and facilitating the generation of reactive oxygen species (ROS) responsible for the degradation of organic pollutants. Furthermore, the specific composition of bioactive molecules in the macroalgal extract can influence the size, shape, and morphology of the synthesized nanoparticles, further modulating their photocatalytic properties.

Furthermore, the high surface area of some of the synthesized NPs, such as the Cu NPs from *S. cervicorne* with surface area of 4.03 m^2/g (Anwar et al., 2021) and the Co-ZnO NPs from *P. capillacea* (15.114 m^2/g) (Meky et al., 2023), contributes to increased active sites for adsorption and catalytic reactions, thereby improving the overall photodegradation efficiency.

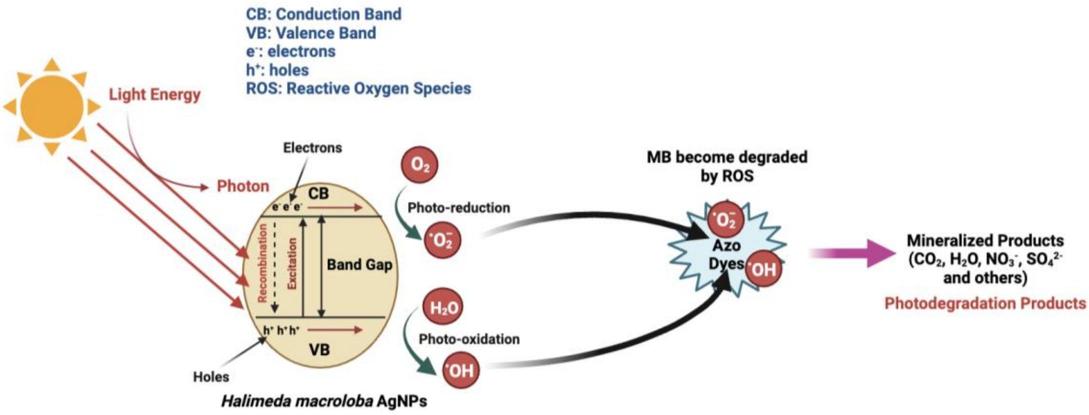

Figure 2. Plausible mechanism of organic azo dyes photodegradation by using the *Halimeda macroloba* AgNPs (The figure fully drawn by BioRender).

To understand the elucidate upon the mechanism of photodegradation of dyes, we can refer to the result reported by Lavanya et al., (2023) and as articulated by Meky et al., (2023). Upon irradiation with visible light, the nanoparticles, acting as photocatalysts, undergo a crucial electronic transition. Photons, carrying energy equal to or greater than the band gap of the silver nanoparticles, excite electrons residing in the valence band. These excited electrons are then promoted to the conduction band, leaving behind electron vacancies known as "holes" in the valence band. Consequent to this excitation, positively charged lacunae, or holes, manifest within the valence band, while the liberated electrons take up residence in the conduction band. These photogenerated electrons, now residing in the conduction band, are highly reactive and readily interact with molecular oxygen adsorbed on the surface of the silver nanoparticles. This interaction leads to the formation of superoxide anion radicals ($•O_2^-$), a highly reactive oxygen species (ROS). Simultaneously, the holes generated in the valence band can oxidize water molecules, leading to the formation of hydroxyl radicals (•OH), another potent ROS. These ROS, generated through the photocatalytic process, play a central role in the degradation of organic pollutants. They can attack the chemical bonds within the dye molecules, breaking them down into smaller, less harmful byproducts. Furthermore, the biomolecules derived from the seaweed Halimeda macroloba, acting as capping agents on the nanoparticle surface, can further enhance the photocatalytic process. These biomolecules, due to their specific interactions with both the nanoparticles and the dye molecules, can act as "bridges," promoting the adsorption of the dye molecules onto the photocatalyst surface. This enhanced adsorption increases the local concentration of the dye molecules near the ROS generated on the nanoparticle surface, thereby accelerating the degradation process.

The research studies highlighted in this review compellingly demonstrate the immense potential of marine macroalgae as a sustainable and environmentally benign resource for the synthesis and stabilization of nanoparticles (NPs) with remarkable photocatalytic activity. These biogenic NPs have exhibited exceptional efficacy in degrading a wide range of persistent organic pollutants, including, but not limited to, azo dyes, nitrophenols, and pharmaceutical compounds, highlighting their potential in addressing critical environmental challenges. The integration of these bio-fabricated NPs into advanced wastewater treatment processes and environmental remediation strategies could pave the way for more sustainable and efficient solutions for addressing organic pollutants in aquatic systems.

CONCLUSION

The utilization of marine macroalgae as stabilizing agents for bio-fabricated nanoparticles in photodegradation applications represents a promising and sustainable approach for environmental remediation. These renewable and abundant marine resources harbor a diverse array of bioactive compounds, such as polysaccharides, proteins, and pigments, which act as effective reducing, capping, and stabilizing agents, bestowing unique properties upon the synthesized nanoparticles. The synergistic interplay between the nanoparticles' inherent photocatalytic capabilities and the antioxidant and redox properties of the macroalgae-derived stabilizers contributes to enhanced photodegradation efficiency against a wide spectrum of organic and inorganic pollutants. Recent studies have demonstrated remarkable photodegradation activities against recalcitrant contaminants like azo dyes, nitrophenols, and pharmaceutical compounds, offering compelling solutions for effective wastewater treatment and environmental decontamination. Aligned with green chemistry principles, the utilization of these marine resources mitigates potential environmental and health concerns while rendering production cost-effective and economically viable. However, challenges persist, including achieving consistent large-scale production, ensuring long-term stability, assessing potential leaching, developing selective systems for specific pollutants, and conducting comprehensive toxicological evaluations. Future research should focus on optimizing synthesis conditions, nanoparticle properties, photodegradation processes, and integrating these systems into existing remediation technologies through collaborative efforts to overcome challenges and unlock the full potential of marine macroalgae-stabilized nanoparticles for sustainable and efficient environmental remediation strategies.

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