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Algal synthesis of metal-based nanoparticles for corrosion protection and adsorption: A review

ABSTRACT

The biosynthesis of metal oxide nanoparticles (MONPs) using algal extracts has gained considerable attention as a green and sustainable strategy for both corrosion protection and adsorption-based remediation. Algal metabolites—particularly polysaccharides, proteins, phenolics and pigments—act as natural reducing, capping and stabilizing agents, offering a renewable alternative to toxic chemical methods. Recent reports highlight that differences in algal species (green, brown, red, and cyanobacteria) significantly influence nanoparticle morphology, crystallinity and surface functionality by subjecting them to characterization techniques; Scanning electron microscopy (SEM), X-ray diffractometer (XRD) and Fourier Transform Infra-red Spectroscopy (FT-IR) respectively,which in turn dictate their protective and adsorptive performance. Advances in ZnO, CuO and Fe_3O_4 nanoparticles synthesized via algal extracts demonstrate notable corrosion inhibition efficiencies (>90% in some acidic and saline environments) through mechanisms such as barrier film formation, charge transfer resistance, and passivation. Parallel studies show high adsorption capacities for heavy metals (Pb^{2+}, Cd^{2+}, Cr^{6+}) and organic dyes, attributed to nanoparticle porosity, surface charge modulation, and bio-derived functional groups. Novel contributions from recent literature emphasize the dual-functionality of these nanomaterials, highlighting not only their corrosion resistance and adsorption efficiency but also their tunability through controlled synthesis parameters such as pH, precursor concentration and algal species selection. Together, these insights position algal-mediated MONPs as promising candidates for eco-friendly material science innovations in corrosion management and wastewater purification technologies.

Keywords: *Algae, Metal oxide nanoparticles (MONPs), Green nanoparticle synthesis, Eco-friendly materials, Corrosion protection, Adsorption, Metal surface coating*

1.0.INTRODUCTION

Corrosion is a natural phenomenon,degrades metals and alloys through chemical or electro-chemical interactions with their environment, posing significant economic and safety risks due to infrastructure deterioration[1].Preventing this phenomenon conventionally has been through coatings, use of sacrificial anodes and corrosion inhibitors, which form protective layers to reduce corrosion rates[2].

The use of green inhibitors, alternatively has shown to be sustainable and ecofriendly[3]. The materials which arederived from higher plant and algae extracts and have gained substantial attention.

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Algae, in particular, are a rich source of bioactive compounds—such as polysaccharides, alkaloids, polyphenols, and proteins—that exhibit excellent corrosion-inhibiting properties. Marine algae have been reported as examples of eco-friendly corrosion inhibitors, particularly in acidic environments[100]. Their metabolites adsorb onto metal surfaces, forming protective barriers that mitigate corrosion in acid media. When incorporated into metal oxide nanoparticles, these compounds not only improve corrosion resistance but also enhance the nanoparticles' adsorption properties, allowing for stronger interaction with metal surfaces [4]. The high surface-area-to-volume ratio of metallic oxide nanoparticles derived from algal extracts further boosts their anti-corrosive efficacy, making them a viable and sustainable alternative to conventional inhibitors [5].

This review focuses on the corrosion inhibitory and adsorption properties ofsome synthesized metal oxide nanoparticles that are derived from algal extracts. The mechanisms and adsorption isotherms, synthesis methods, and the potential self-healing capabilities of these metal oxide nanoparticles are explored. Also detailed are the classification and preparation of algae extracts, the nature of organic and green inhibitors and the characterization of synthesized metaloxide nanoparticles underscores the potential of algae-based materials as corrosion inhibitors.

1.1.Anti-Corrosion of Metal Oxide Nanoparticles

The anti-corrosion properties of metal oxide nanoparticles stem from their ability to form a protective barrier that prevents metal interaction with corrosive agents. Algae-synthesized metal oxide nanoparticles, particularly those incorporating bioactive compounds, provide superior corrosion protection compared to algae alone because of their strong adsorption properties and high surface reactivity[6]. MO-NPs such as ZnO, Mn_2O_3, and TiO_2 primarily inhibit corrosion through barrier formation and adsorption, reducing the diffusion of corrosive species. In composite materials, their incorporation further enhances protection by modifying electrochemical properties. For example, polypyrrole (PPy)-TiO_2 composites function as diffusion barriers while forming heterojunctions that obstruct charge transport, thereby significantly inhibiting electrochemical corrosion processes. These composites surpass single-component systems by integrating both physical and chemical protection; however, challenges related to nanoparticle stability and environmental impact remain key areas for further optimization [7].

Also, metal oxide nanoparticles (MO-NPs), such as ceria (CeO_2), exhibit unique redox-based corrosion protection mechanisms. Ceria adsorbs onto metal surfaces, forming passive layers that stabilize corrosion potential and suppress electrochemical activity. This behaviour is driven by the dynamic redox cycling between Ce^{4+} and Ce^{3+}, which facilitates passivation under both oxidative and reductive conditions. Experimental studies have shown that ceria nanoparticles create a "blocking electrode" effect, reinforcing the metal surface and significantly enhancing its resistance to corrosion [8].

When incorporated into composite materials, MO-NPs exhibit synergistic effects that significantly enhance both corrosion resistance and overall material performance[9]. In polyimide-based systems, the inclusion of TiO_2 and carbon nanotubes improves thermal stability, stiffness, and durability by modifying the polymer matrix and passivation degradation by-products. In particular, carbon nanotube fillers in biphenyl-based polymer systems create microcavities that facilitate the controlled release of degradation products, while TiO_2 enhances overall structural stability. Similarly, composites based on pyromellitic dianhydride-oxydianiline, reinforced with CeO_2 and nanocarbon mixtures, demonstrate improved thermal resistance by altering the matrix structure and inhibiting oxidative reactions. These interactions underscore the multifunctional role of metal oxide nanoparticles in composite materials [10].

Although, carbon dioxide (CO_2) gas itself is non-corrosive, its interaction with water leads to the formation of carbonic acid (H_2CO_3), which significantly accelerates metal corrosion. The electrochemical reaction between carbonic acid and metal involves a cathodic hydrogen evolution process, emphasizing the necessity of protective layers, such as those formed by metal oxide nanoparticles (MO-NPs), in mitigating corrosion in such aggressive environments.

The overall reaction governing this process is:

$$Fe(s) + CO_2(aq) + H_2O(l) \rightarrow Fe^{2+}(aq) + CO_3^{2-}(aq) + H_2(g) \quad (1)$$

The anodic reaction involves the oxidation of iron:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad (2)$$

The cathodic reactions include the reduction of protons and other species:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad (3)$$

$$2H_2CO_3(aq) + 2e^- \rightarrow H_2(g) + 2HCO_3^-(aq) \quad (4)$$

$$2HCO_3^-(aq) + 2e^- \rightarrow H_2(g) + 2CO_3^{2-}(aq) \quad (5)$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (6)$$

The corrosion process of CO_2 in a water-rich environment initiates with the formation of an iron carbide (Fe_3C) framework within the steel substrate during the initial dissolution stage. Subsequently, iron carbonate ($FeCO_3$) deposits on the surface, while carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions diffuse inward, reacting with the steel matrix to form an intermediate layer and an inner protective layer[11].

1.2. Metal Oxide Nanoparticles Derived from Biological Sources

Numerous studies have highlighted the significance of biological species such as plants, microorganisms, and algae in the synthesis of MO-NPs, demonstrating their effectiveness as both reducing and stabilizing agents.Phytochemicals, including terpenoids, flavonoids, and polyphenols, act as natural reducing and stabilizing agents, facilitating nanoparticle formation. This biosynthetic approach is valued for its simplicity, scalability, and ability to produce nanoparticles with distinctive bioactive properties. For instance, zinc oxide nanoparticles synthesized using Dovyalis caffra leaf extracts have exhibited remarkable antioxidant and anticancer properties, surpassing the efficacy of individual metal oxides in targeted applications [12].

Additionally, the phyto-mediated synthesis of zinc oxide nanoparticles (ZnO-NPs) using *Berberis aristata* leaf extracts has demonstrated significant antibacterial and antioxidant properties. These MO-NPs have proven particularly effective against urinary tract pathogens such as *Escherichia coli* and *Staphylococcus aureus*, highlighting their potential for biomedical applications [13]. Similarly, iron oxide nanoparticles derived from the stem bark and root of *Moringa oleifera* showed some activities against a malaria pathogen[14].

Meanwhile, copper oxide nanoparticles (CuO-NPs) synthesized through green methods using plant extracts have shown considerable promise in environmental remediation and catalytic applications. Their high surface reactivity enhances their effectiveness in pollutant degradation and catalytic efficiency, further emphasizing the versatility of bio-derived metal oxide nanoparticles in sustainable technological advancements [15]. Nickel oxide nanoparticles (NiO-NPs) synthesized via plant-derived phytochemicals revealed that these nanoparticles exhibit enhanced electro-chemical and catalytic properties compared to chemically synthesized alternative materials[16].

Meanwhile, microbial systems, including bacteria and fungi, are instrumental in the biosynthesis of metal oxide nanoparticles. The unique enzymatic machinery of microbes enables the reduction of metal ions to metal nanoparticles while maintaining precise control over particle morphology. For example, bacterial synthesis of metal nanoparticles has been leveraged to produce gold, silver, and selenium nanoparticles with biomedical and catalytic potential [17]. Fungi like Aspergillus spp. are noted for their ability to synthesize metal nanoparticles at higher yields, underscoring their scalability for industrial applications.

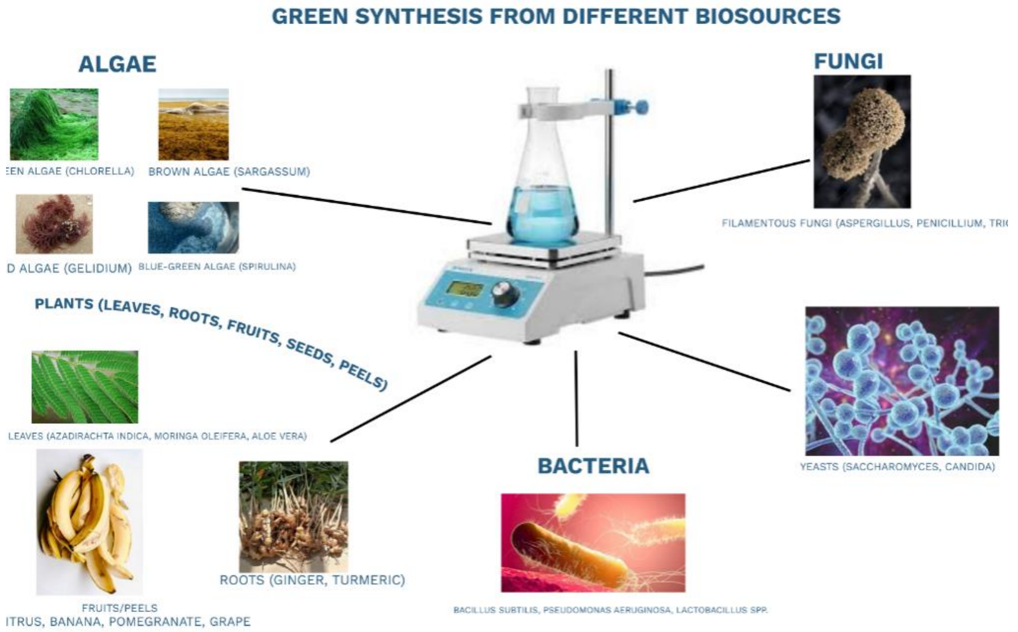

Figure 1. Eco-friendly synthesis from different biological sources

1.3. Preparation and Applications of Algae Extracts

Algae represent an incredibly diverse group of photosynthetic organisms, classified into several groups based on differences in pigmentation, biochemical composition, and evolutionary lineage. Green algae, for example, are characterized by the presence of chlorophyll-a and chlorophyll-b, along with β-carotene. The latter serves not only as a pigment but also as a renewable energy reserve that supports vital metabolic processes in the cell [18]. Algal species like *Chlorella* and *Spirulina* are particularly notable for their high protein content—often surpassing 50% of their dry weight—making them valuable as alternative protein sources for both human nutrition and industrial applications [19].

Brown algae, on the other hand, contain the accessory pigment fucoxanthin in addition to chlorophylls. Fucoxanthin has a unique molecular structure that endows it with potent antioxidant properties, including the ability to neutralize free radicals and reduce oxidative stress [20].

Furthermore, brown algae are rich in several bioactive polysaccharides such as alginates, laminarin, and fucoidan. Each of these compounds offers distinctive biological functions: alginates are widely used for their gelling and stabilizing properties [21], laminarin has been studied for its immunomodulatory effects [22], and fucoidan exhibits a range of bioactivities, including anti-inflammatory and anticancer potential [23].

Red algae (Rhodophyta) also contribute significantly to the bioactive potential of algal biomass. They are rich in pigments such as phycoerythrin and phycocyanin, which are not only valued for their vivid coloration but also for their water solubility and strong gel-forming capacity[24].

The method of extraction used to isolate these valuable biomolecules greatly influences both their yield and functional quality. Solvent extraction, which employs organic solvents like ethanol, methanol, or hexane, remains one of the most common approaches. Although relatively time-consuming, it effectively isolates lipids, pigments, and other targeted molecules from algal biomass [25]. In recent years, advanced techniques such as Microwave-Assisted Extraction [26], Ultrasound-Assisted Extraction [27], Enzyme-Assisted Extraction [28], and Supercritical Fluid Extraction have gained traction for their ability to enhance extraction efficiency and reduce environmental impact [25].

Beyond their nutritional and therapeutic value, algal extracts play a pivotal role in nanotechnology. They act as natural reducing and capping agents in the green synthesis of metal oxide nanoparticles. These eco-friendly methods have been particularly successful in producing nanoparticles like silver (Ag) and copper oxide (CuO), which demonstrate potent antimicrobial, antifungal, and catalytic properties [29]. Additionally, specific components of algae such as fucoidan and alginates have shown biomedical potential with anticoagulant, antiviral, and immune-modulating effects, making them promising candidates for drug development [30].

Algal extracts also contribute significantly to the field of renewable energy. In particular, hydrothermal liquefaction—a process that converts algal biomass into bio-oil—has seen enhanced efficiency when combined with organic solvent extraction and catalytic upgrading techniques. These innovations have led to increased energy yields and have reinforced the role of algae as a feasible source of sustainable biofuel. Meanwhile, in the domain of functional foods, algae-derived pigments like phycobiliproteins offer antioxidant benefits as natural food colorants, and sulphated polysaccharides have shown promise in promoting gut health and strengthening immune function. Such wide-ranging applications underscore the growing relevance of algal extracts in sustainable biotechnology and public health [27].

2.0. SYNTHESIS OF ALGAL-MEDIATED METAL OXIDE NANOPARTICLES

The synthesis of metal oxide nanoparticles (MONPs) using algal biomass is a nuanced and environmentally friendly process that can involve live algae, dried biomass, or aqueous algal extracts. When solutions containing metal precursors—such as copper nitrate ($Cu(NO_3)_2$) or zinc chloride ($ZnCl_2$)—are introduced to algal extracts, a series of biologically mediated reduction reactions takes place. Several key parameters, including the pH of the solution, the ambient temperature, and the presence of light, are meticulously adjusted to control the characteristics of the resulting nanoparticles. For instance, elevated temperatures and optimal pH levels generally improve the rate and efficiency of metal ion reduction, while exposure to light can enhance the photocatalytic activity of certain algal metabolites [31]..

A crucial factor in this biosynthesis process is the location where the nanoparticles form—either inside the algal cells (intracellular) or in the surrounding solution (extracellular). In intracellular synthesis, metal ions enter the algal cells, where they are reduced into nanoparticles through interactions with intracellular enzymes and metabolites. In contrast, extracellular synthesis depends on the presence of bioactive compounds secreted into the extract, which reduce metal ions in the external medium. Enzymes such as nitrate reductase, along with compounds like phenolics and flavonoids, function as electron donors, driving these redox reactions and facilitating the transformation of metal ions into nanoscale oxides [32].

A practical example of this approach is seen in the use of *Spirulina platensis*, a blue-green microalga, for the biosynthesis of copper oxide nanoparticles. These nanoparticles have displayed considerable antibacterial and anticancer properties, effects that are closely linked to the biologically active compounds present in the algal extract. These biomolecules not only assist in reducing the metal ions but also stabilize the formed nanoparticles, enhancing their functionality and biocompatibility [33].

The biochemical richness of algae provides a versatile platform for the synthesis of a variety of metal oxide nanoparticles, each possessing unique functional traits. For example, brown algae such as *Sargassum wightii* have been successfully used to produce cerium oxide (CeO_2) nanoparticles, which are known for their robust antioxidant activity [34].

Similarly, green algae like *Ulva intestinalis* have facilitated the green synthesis of zinc oxide (ZnO) nanoparticles, which exhibit strong antimicrobial effects and are well-suited for applications in water purification technologies [35].

The synthetic mechanism of algae-mediated MONPs revolves around redox reactions facilitated by the bioactive constituents within the algae[36]. These biomolecules—ranging from proteins and polysaccharides to flavonoids and polyphenols—not only act as reducing agents but also stabilize the nanoparticles, preventing their agglomeration and ensuring long-term stability. Algae thus serve as highly efficient natural factories for producing a wide array of nanoparticles, including but not limited to gold, silver, zinc oxide, and copper oxide, each tailored for specific industrial, biomedical, or environmental applications [37].

2.1. Algae-Mediated Metal Oxide Nanoparticles

Many metal oxide nanoparticles have been synthesized using different algae extracts. Scientists have increasingly reported this category of materials describing their morphology, ascertaining other properties and applied them for different purposes. Table 1 itemized some reported algae-mediated metal oxide nanoparticles with their benefits.

Table 1. Sources and Benefits of Some Algae-Mediated Metal Oxide Nanoparticles

Metal (s)	Algae Source	Shape and Size	Benefits	Ref.
Copper Oxide (CuO)	Coelastrellaterrestris	Flattened rice-like structure, 4-50 nm	Photocatalytic dye degradation	[38]
Zinc Oxide (ZnO)	*Ulvafasciata*	Spherical, 3-33 nm	Antibacterial and catalytic activities	[39]
Silver (Ag)	*Chlorella pyrenoidosa*	Spherical, 5–20 nm	High antibacterial efficacy, photocatalytic properties for wastewater treatment.	[40]
Zinc Oxide (ZnO)	*Lyngbya majuscule*	Rod-shaped, 20–70 nm	Antibacterial properties with environmental safety and cost-effective synthesis.	[41]
Iron Oxide (Fe_3O_4)	Padinapavonica	Spherical, 10-19.5 nm	Heavy metal removal / adsorption	[42]
Iron Oxide (Fe_3O_4)	Colpomeniasinuosa, Pterocladiacapillacea	Spherical, 15–60 nm	Effective antimicrobial action, spherical nanoparticles for biomedical applications.	[43]
Copper Oxide (CuO)	*Sargassumwightii*	Spherical, 10–30 nm	Antibacterial properties, high biocompatibility.	[44]
Gold, Silver (Au, Ag)	*Spirulina platensis*	Spherical, 10–40 nm	Efficient reduction of metals to nanoparticles, biocompatibility, and enhanced biosensing capabilities.	[41]
Titanium, Zinc (TiO_2, ZnO)	*Pseudokirchneriellasubcapitata*	Rod-shaped, 20–100 nm	Photocatalytic and anti-algal activity, stable nanostructures for environmental safety.	[41]
Noble Metals (Au, Pt)	*Anabaena flosaquae*	Spherical, 5–20 nm	Scalable synthesis, application in energy and environmental nanotechnology.	[45]
Gold (Au)	*Galaxauraelongata*	Spherical, 3.85–77.13 nm	Efficient antibacterial activity, spherical nanoparticles with sizes ranging from 3.85 to 77.13 nm.	[46]
Silver Chloride (AgCl)	*Sargassumplagiophyllum*	Spherical, 5–15 nm	Spherical nanoparticles with antimicrobial and catalytic activities.	[47]
Silver (Ag)	*Oscillatorialimnetica*	Quasi-spherical, 3.3–17.97 nm	Quasi-spherical nanoparticles with high antibacterial activity, average size of 3.3 to 17.97 nm.	[48]
Silver (Ag)	*Caulerparacemosa*	Spherical and triangular nanoparticles (5-50 nm)	Spherical and triangular nanoparticles with antimicrobial and catalytic properties.	[49]

Zinc Oxide (ZnO)	*Ulvafasciata*	Spherical, 20–100 nm	Spherical nanoparticles for food preservation, high antibacterial and quality-preserving properties for shrimp.	[50]
Gold (Au)	*Turbinariaconoides*	Spherical and triangular, 10–50 nm	Triangular, spherical, and pseudo-spherical nanoparticles for biomedical and environmental applications.	[51]
Iron Oxide (Fe_3O_4)	*Janiarubens*	Spherical, 15–40 nm	Spherical nanoparticles with strong antibacterial activity and potential for biofilm disruption.	[52]
Silver (Ag)	*Portieriahornemannii*	Spherical, 10–30 nm	Spherical nanoparticles with antimicrobial properties against fish pathogens.	[53]
Silver (Ag)	*Gelidiumamansii*	Spherical, 27-54 nm.	Bactericidal activity against biofilm-forming pathogens, potential application in anti-fouling coatings.	[54]
Gold (Au)	*Rhizoclonium sp.*	Monodisperse, 5–25 nm	Monodisperse gold nanoparticles with potential applications in industrial catalysis and medical imaging.	[55]
Zinc Oxide (ZnO)	*Tetraselmissuecica*	Rod-shaped nanoparticles (10-30 nm)	Non-toxic to marine algae, showcasing low environmental impact during nanoparticle synthesis.	[56]
Silver (Ag)	*Acutodesmusdimorphus*	Spherical, 2-20 nm	Strong antioxidant activity, nanoparticles synthesized from de-oiled biomass.	[57]
Gold and Silver (Au, Ag)	*Chlorella pyrenoidosa*	Spherical nanoparticles (15-20 nm)	Biosynthesized under controlled pH and temperature conditions, suitable for eco-friendly applications.	[58]
Silver (Ag)	*Desmodesmus sp.*	Spherical, 3-30nm	Strong antibacterial and antifungal activity, suitable for biomedical applications.	[59]
Silver (Ag)	*Oscillatoriawillei*	Spherical, 100-200 nm	Strong antimicrobial activity, stable nanoparticle synthesis.	[60]
Iron Oxide (Fe_3O_4)	*Sargassumplagiophyllum*	Spherical, 54-78nm.	Antimicrobial and antioxidant activity.	[61]
Silver (Ag)	*Spirulina platensis*	Spherical, 5-30 nm	Antimicrobial and catalytic activity, eco-friendly synthesis.	[62]
Gold (Au)	*Chlorella vulgaris*	Spherical nanoparticles (10-25 nm)	Biosynthesis of stable gold nanoparticles with unique optical properties for biomedical uses.	[63]
Palladium (Pd)	*Chlorella vulgaris*	Spherical, 5-20 nm	Electrocatalytic properties for industrial use.	[64]
Zinc Oxide (ZnO)	*Ulva intestinalis*	Spherical nanoparticles (20-40 nm)	Antimicrobial properties and application in water treatment.	[65]
Palladium (Pd)	*Plectonemaboryanum*	Spherical, 1-20 nm	Biosynthesis of catalytic nanoparticles for fuel cell applications.	[66]
Gold (Au)	*Plectonemaboryanum*	Spherical, 2-16 nm	Biosynthesis of catalytic nanoparticles for fuel cell applications.	[67]
Copper Oxide (CuO)	*Sargassumlongifolium*	Spherical nanoparticles (20-50 nm)	Antioxidant and antibacterial properties.	[68]

Silver	*Padinatetrastromatica*	Spherical, 20 nm	Antioxidant and antibacterial properties.	[69]
Silver (Ag)	*Dunaliellasalina*	Spherical, 5–15 nm	Size-controlled nanoparticle synthesis for enhanced antimicrobial activity.	[70]
Gold (Au)	*Sargassumtenerrimum*	Plate-shaped, 30–70 nm	Plate-shaped nanoparticles with applications in optoelectronics and catalysis.	[71]
Titanium dioxide (TiO_2)	*Bostrychiatenella, Laurencia obtuse, Halimeda tuna Sargassumfilipendul*	uniform with small crystal,10 – 50 nm	Antifouling Coating	[72]
Titanium dioxide (TiO_2)	*Spirulina platensis*	Irregularly dispersed and spherical, 90-150 nm		[73]
Titanium dioxide (TiO_2)	*Elodea canadensis*	Spherical, 22 nm		[74]
Magnesium Oxide (MgO)	Cystoseiracrinita	Spherical, 3-18 nm	Antimicrobial, Cytotoxicity, Larvicidal applications	[75]
Magnesium Oxide (MgO)	Sargassumwightii	cubic crystalline structure, 68.06 nm	Antimicrobial, Cytotoxicity, catalytic	[76]
Magnesium Oxide (MgO)	Spirulina platensis	Spherical, 30-40 nm	Antibacterial	[77]

2.2. Characterization of Algal-based Metal Oxide Nanoparticles

One of the most commonly employed methods for evaluating the crystalline structure of MONPs is X-ray diffraction (XRD). This technique has been extensively used to analyze nanoparticles such as zinc oxide (ZnO) and titanium dioxide (TiO_2) synthesized using green algae, confirming their phase purity and crystallite size[78]. For instance, XRD analysis of copper oxide (CuO) nanoparticles derived from *Bifurcaria bifurcata* (a brown algae) has revealed particle sizes ranging from 5 nm to 45 nm. These findings highlight the impact of reaction conditions on nanoparticle crystallinity, demonstrating the importance of precise control during synthesis[79].

Fourier-transform infrared spectroscopy (FTIR) plays a key role in identifying functional groups involved in nanoparticle synthesis. Studies on copper oxide (CuO) nanoparticles synthesized using Macrocystis pyrifera brown algae have shown strong interactions between proteins and polysaccharides, confirming their role as natural reducing and stabilizing agents [80]. Similarly, FT-IR analysis of algal-derived iron oxide (Fe_3O_4) nanoparticles has detected characteristic peaks for hydroxyl and carboxyl groups, highlighting the involvement of biomolecules in the synthesis process [81].

Microscopic techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provide valuable insights into the shape, size, and distribution of MO nanoparticles. SEM imaging of algae-mediated CuO nanoparticles has revealed a predominantly spherical shape with uniform size distribution[35]. TEM analysis further confirms the formation of well-defined nanoparticles, while energy dispersive X-ray spectroscopy (EDS) verifies their elemental composition, ensuring the accuracy of synthesis methods.

Ultraviolet-visible (UV-Vis) spectroscopy is commonly used to investigate the electronic properties of MONPs. Research on zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles synthesized through algal-mediated processes has shown strong absorption peaks in the UV region, supporting their applications in photocatalysis[82]. However, studies examining the impact of these MO nanoparticles on Pseudokirchneriella subcapitata algae under UV irradiation conditions suggest potential phototoxic effects, highlighting the need for controlled and responsible applications [83]. The integration of toxicity assessments in MONPs characterization is crucial to ensuring their environmental safety.

To assess MO nanoparticle stability and dispersion behaviour in various mediums, dynamic light scattering (DLS) and zeta potential measurements are commonly employed. These analyses determine surface charge and aggregation tendencies, which are critical for applications in aqueous and industrial environments.

Electrochemical techniques, such as cyclic voltammetry and electrochemical impedance spectroscopy, have gained importance in evaluating the corrosion inhibition potential of

MONPs. Recent studies indicate that algae-mediated cerium oxide (CeO_2) and ZnO nanoparticles enhance corrosion resistance by forming self-repairing passive layers, as confirmed by impedance spectroscopy[84]. These findings underscore the growing interest in MONPs as sustainable and efficient materials for protective coatings and industrial applications.

By integrating multiple characterization techniques, researchers can optimize the synthesis and application of algae-derived MONPs, ensuring both performance efficiency and environmental compatibility.

2.3. Factors Affecting the Synthesis of Algal-Based Metal Oxide Nanoparticles

The algal-mediated synthesis of metal oxide nanoparticles (MONPs) is a complex process influenced by a range of environmental and physicochemical parameters. These factors critically determine the nanoparticles' size, shape, crystallinity, and overall functionality, making their control essential for tailoring specific properties.

One of the earliest steps in this biosynthesis process is the careful adjustment of temperature and reaction time. Higher temperatures typically accelerate the reduction of metal ions, promoting the formation of well-crystallized nanoparticles. However, temperatures that exceed the optimal threshold can induce aggregation, reducing the structural integrity and dispersion of particles. For instance, moderate temperature conditions were found to be ideal during the synthesis of copper oxide (CuO) nanoparticles using brown algae, where algal proteins served as effective capping agents to maintain nanoparticle stability [80].

Following temperature control, the ratio of algal biomass to metal precursors plays a crucial role in determining nanoparticle yield and morphology. A higher biomass concentration provides an abundance of functional groups, such as hydroxyl and carboxyl moieties, which aid in the reduction and stabilization of nanoparticles. Conversely, an excessive concentration of metal precursors can result in rapid nucleation and subsequent aggregation. This balance has been particularly critical in the synthesis of zinc oxide (ZnO) nanoparticles, where optimizing the biomass-to-precursor ratio significantly enhanced their antimicrobial performance [85].

Light exposure is another key factor, particularly due to algae's phototrophic nature. Variations in light intensity and wavelength directly affect the production of bio-reductants such as chlorophylls and carotenoids. These compounds not only contribute to metal ion reduction but also influence the quality of the final nanoparticle structure. Studies have demonstrated that light-induced photochemical reactions can enhance the crystallinity and uniformity of metal oxide nanoparticles like titanium dioxide (TiO_2) and ZnO [86].

pH is equally critical in shaping nanoparticle properties. Alkaline conditions tend to promote faster reduction reactions, leading to the formation of smaller and more homogeneous nanoparticles. In contrast, acidic environments often slow the reduction process and increase the risk of aggregation. This relationship has been validated in the synthesis of iron oxide nanoparticles (IONPs), where pH optimization improved both magnetic and catalytic performance [35].

Algae's biochemical makeup also plays an intrinsic role. Secondary metabolites such as phenols, flavonoids, and terpenes act as natural reducing and stabilizing agents, regulating both the kinetics of nanoparticle formation and their final morphology. For example, phenolic compounds have been found to enhance the surface functionalization and stability of silver oxide nanoparticles, contributing to their biological efficacy [87]

Post-synthesis calcination is employed to improve the structural properties of the synthesized nanoparticles. Controlled heat treatment, particularly in the case of cerium oxide (CeO_2) nanoparticles, has been shown to refine crystallinity and alter phase composition. This step increases the number of surface defects, thereby enhancing the antioxidant properties of the nanoparticles [88].

2.4. Mechanisms of Synthesis of Algae-Mediated Metal Oxide Nanoparticles

The biosynthesis of metal oxide nanoparticles (MONPs) via algae begins with the reduction of metal ions, a process fundamentally driven by bioactive compounds present in algal cells and extracts. Flavonoids, polyphenols, and enzymes act as electron donors that reduce metal ions such as Fe^{3+}, Zn^{2+}, and Ce^{4+} into their corresponding metallic or oxide forms. This reduction marks the initiation of nanoparticle formation, setting the stage for nucleation—the emergence of tiny, reactive clusters formed from reduced metal atoms. During this phase, biomolecules in the algal matrix play a dual role: not only facilitating the reduction reaction but also stabilizing these emerging clusters to regulate their growth. For example, in the synthesis of zinc oxide (ZnO) nanoparticles using *Spirogyra hyalina*, algal proteins and polysaccharides contribute both to the enzymatic reduction of zinc ions and to the capping of the formed nanoparticles, thereby preventing their aggregation [89].

As nucleated nanoclusters grow, they undergo oxidation and crystallization, critical stages that define the physicochemical properties of the final nanoparticles. The oxidation process, often involving ambient oxygen from water or air, is accelerated by enzymes and proteins in the algal extract. These biomolecules influence the rate and extent of oxidation, which in turn governs the crystalline structure that the nanoparticles ultimately adopt. In the case of titanium dioxide (TiO_2) nanoparticles, enzymatic activity from algal sources has been shown to promote the formation of the anatase crystalline phase—renowned for its superior photocatalytic capabilities [90]. This controlled oxidation and crystallization process underscores the importance of reaction conditions such as pH, temperature, and the concentration of bio-reductants in shaping the structure and functionality of MONPs.

The structural evolution of these nanoparticles continues through a regulated assembly process. Reduced metal atoms gradually coalesce into nanoclusters, which are further guided by algal biomolecules into organized, well-defined morphologies. Proteins, lipids, and other organic compounds in algae serve as capping agents during this stage, determining particle shape and size while simultaneously ensuring colloidal stability. In the biosynthesis of cerium oxide (CeO_2) nanoparticles using *Spirulina platensis*, these bioactive compounds not only facilitated the reduction of cerium ions but also directed the controlled growth of nanoparticles. The resulting CeO_2 structures demonstrated high crystallinity and potent antioxidant activity, reflecting the critical influence of algal-derived molecules on nanoparticle quality and performance [91].

Capping and stabilization are the final but essential steps in the algal-mediated synthesis of MONPs. Once nanoparticles are formed, their surfaces are coated with organic molecules from the algae, which prevent uncontrolled aggregation via electrostatic and steric mechanisms. This capping layer maintains nanoparticle dispersion and enhances their compatibility in biological environments. Moreover, the surface chemistry imparted by these natural stabilizers significantly affects the catalytic and optical properties of the nanoparticles. For instance, in ZnO nanoparticle synthesis, algae-derived proteins serve as effective stabilizers, contributing to enhanced antimicrobial activity by modulating the nanoparticle's surface interactions with microbial membranes [92]. These stabilization processes not only preserve the metal oxide nanoparticle functionality but also broaden their applicability in biomedical and environmental domains.

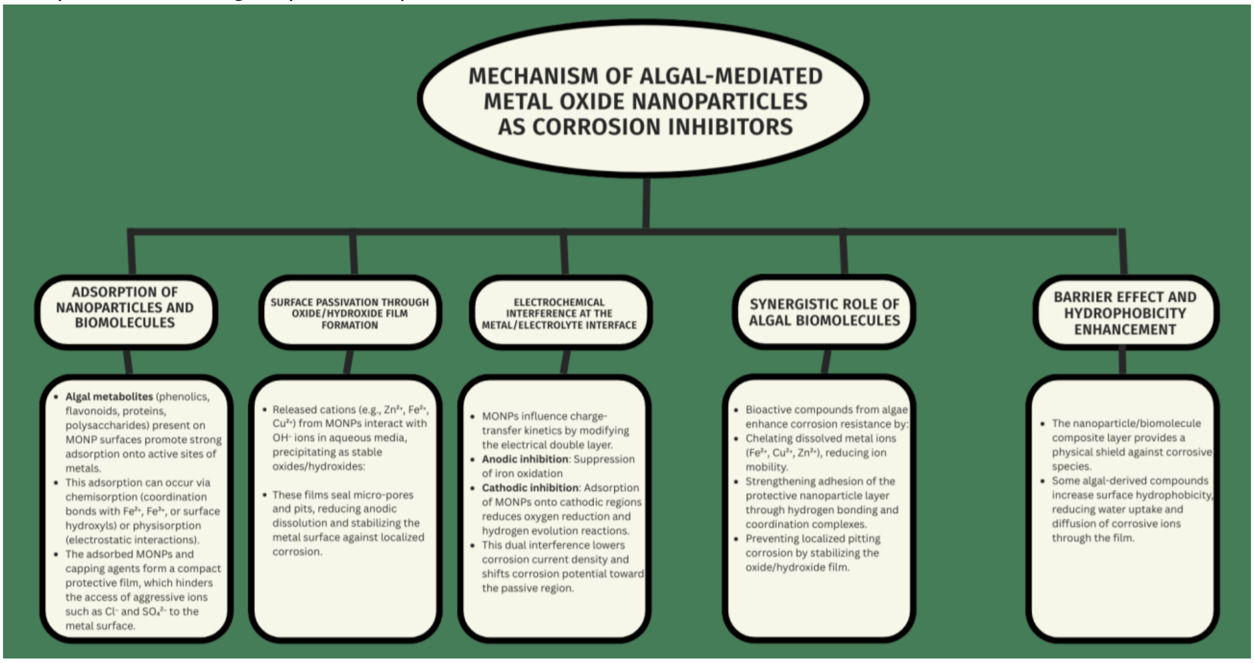

Figure 2. Mechanism of Algae-mediated Metal Oxide Nanoparticles as Corrosion Inhibitors

3.0. ALGAE-MEDIATED METAL OXIDE NANOPARTICLES AS CORROSION INHIBITORS, ADSORPTION POTENTIAL AND MECHANISMS

Corrosion inhibitors play a crucial role in preventing or slowing down the degradation of metals in various environmental conditions. These substances can be classified according to their chemical structure, functional mechanisms, or the specific conditions under which they operate. One prominent class includes adsorption inhibitors, which function by forming a protective film over metal surfaces through physical or chemical interactions, thereby preventing exposure to corrosive elements. In algae-mediated metal oxide nanoparticles (MONPs), bioactive compounds such as proteins, flavonoids, and polysaccharides serve as natural capping agents. These biomolecules stabilize the nanoparticles and facilitate the formation of a robust protective barrier that mitigates metal corrosion through adsorption processes.

Among these, zinc oxide nanoparticles (ZnONPs) synthesized using green algae like Gracilaria edulis have shown notable efficacy in corrosion protection. These nanoparticles adhere uniformly to metallic surfaces and form durable monolayer films that block corrosive agents. The adsorption behavior of ZnONPs follows the Langmuir isotherm model, indicating the formation of a homogeneous monolayer, which enhances their protective efficiency against corrosion [93].

Further investigations into MONPs derived from Codium macroalgae reveal their dual functionality as both adsorbents and corrosion inhibitors. These nanoparticles, rich in natural bioactives, exhibit strong adherence to metal surfaces and form stable, protective layers that prevent environmental degradation. The adsorption process of these materials, assessed through both Langmuir and Freundlich isotherms, confirms their high surface affinity and strong potential for corrosion inhibition in demanding industrial environments [94].

Beyond corrosion protection, algae-mediated MONPs have demonstrated significant capabilities in environmental remediation, particularly in dye adsorption from wastewater. Studies involving nanoparticles synthesized from Arthrospira platensis and Pterocladia capillacea have shown that adsorption performance is influenced by multiple factors, including initial dye concentration, nanoparticle dosage, solution pH, temperature, and contact time. Higher dye concentrations enhance adsorption capacity due to increased diffusion forces, though efficiency may decline at saturation levels. Optimal nanoparticle dosage increases surface area availability, while excessive amounts can lead to particle agglomeration, reducing active surface sites.

Solution pH plays a pivotal role in adsorption behavior. For cationic dyes like methylene blue (MB), acidic to neutral pH conditions favor electrostatic interactions with negatively charged nanoparticle surfaces. Conversely, anionic dyes such as IV2R exhibit maximum adsorption at lower pH levels, where nanoparticles acquire a positive surface charge. Temperature further contributes to adsorption kinetics; elevated temperatures enhance dye diffusion and activate more surface binding sites, consistent with an endothermic process. Most dye adsorption occurs within the first 10–15 minutes, indicating rapid surface saturation followed by gradual equilibrium.

Isotherm modeling (Table 2) confirms that the Langmuir and Dubinin–Radushkevich models most accurately describe the monolayer, physical adsorption behavior of these nanoparticles with higher values of R-square.These findings affirm that algae-mediated MONPs not only serve as sustainable corrosion inhibitors but also possess high adsorption capacities and surface modifiability, making them effective tools in dye remediation efforts [95,96].

Supporting this, ZnO nanoparticles synthesized using Padina pavonica demonstrated strong adsorption and photocatalytic degradation capabilities toward methylene blue, highlighting their usefulness in wastewater treatment applications [97]. Similarly, ZnO nanoparticles produced with extracts from Ulva fasciata, a green macroalga, were effective in removing organic pollutants from tannery wastewater [39]. MONPs derived from Arthrospira platensis followed pseudo-second-order kinetics and Langmuir isotherm behavior during methylene blue adsorption, indicating chemisorption on a homogeneous surface with high affinity and selectivity [95].

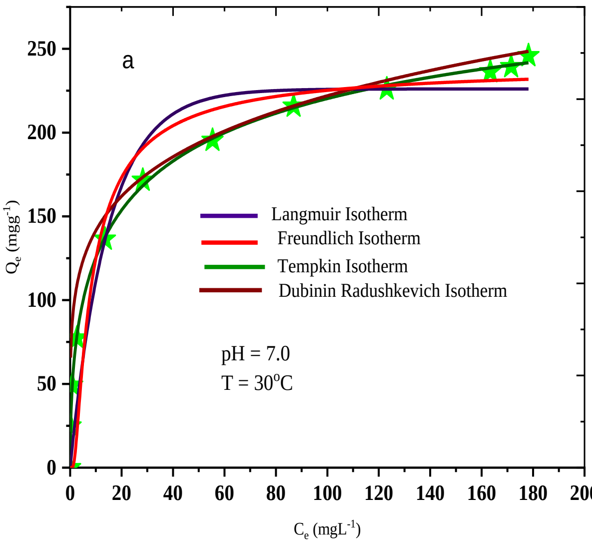

Figure 3: Isotherm Plots

In addition, the development of hybrid nanomaterials by combining ZnO nanoparticles with algal biomass from Sargassum has shown synergistic advantages. This composite material demonstrated immediate and effective absorption and degradation of malachite green dye, underscoring its potential as a multifunctional agent for water purification [98].

Although metal oxide nanoparticles (MONPs) have demonstrated significant potential for corrosion protection, their application in this field remains underexplored. Existing research is largely concentrated on other functionalities such as antimicrobial studies, making them highly suitable for biomedical applications [99]. Furthermore, the global urgency surrounding antibiotic resistance has driven much of the scientific focus toward algae-based nanoparticles for antimicrobial, anticancer, and drug delivery purposes, often at the expense of corrosion-related research[87].

Nonetheless, a limited number of studies have begun to highlight the corrosion-inhibiting potential of algae-derived MONPs. Notably, hybrid coatings incorporating ZnO and CuO nanoparticles synthesized from *Sargassum muticum* (a brown algae) have demonstrated substantial anti-corrosion and anti-biofilm activity on mild steel, with inhibition efficiencies reaching as high as 92.3% in acidic environments[100]. These findings indicate a promising avenue for the development of sustainable, multifunctional corrosion inhibitors based on algal nanomaterials. Moreover, certain algae have intrinsic capabilities to form biofilms that restrict oxygen diffusion and shield metal surfaces, thereby reducing the electrochemical processes that lead to corrosion [101].

Table 2. Isotherm models applied for the adsorption of studies

Name	Model
Langmuir	$Q_{eq} = \frac{Q_{max} b C_e}{1 + b C_e}$ (7) Qeq and Qmax are the amounts (mg/g) of dye adsorbed per unit mass of adsorbent and maximum adsorption capacity at equilibrium, respectively, Ce is the equilibrium concentration of adsorbate, while b (L mg-1) Langmuir constant.
Freundlich	$Q_{eq} = K_F C_e^{1/n}$ (8) KF(mg g-1) (L mg-1)1/n is a rough estimation of adsorption capacity of the adsorbent, 1/n is the adsorption intensity.
Tempkin	$Q_e = \frac{RT}{b_T} \ln a_T C_e$ (9) R (J molK-1) is the gas constant, T (K) is absolute temperature, aT (mg L-1) is the binding constant and bT (L g-1) is related to the heat of adsorption
Dubinin–Radushkevich	$Q_e = Q_s e^{-\beta \varepsilon^2}$ *(10)* Qs (mg g-1) is the saturation capacity, β (mol J)2 is a constant relation to adsorption energy while ε is related to the mean free energy of adsorption and given $\varepsilon = RT * \ln\left(1 + \frac{1}{C_e}\right)$

Corrosion rate

$$(g/h/cm^2) = \frac{\Delta w}{At} \quad (11)$$

where Δw is the weight loss in milligrams of the coupons before and after in immersion(g), *A* is the surface area of the metal coupon in (cm^2), t is the period of immersion in hours.

Inhibition efficiency

$$(IE\ \%) = \left(\frac{W_0 - W_1}{W_0}\right) \times 100 \quad (12)$$

$$Surface\ Coverage\ (\theta) = \left(\frac{W_0 - W_1}{W_0}\right) \quad (13)$$

where W_0 and W_1 represent the weight losses of the steel in the absence and presence of the Zn-O nanoparticles, respectively.

Table 3. Adsorption Isotherms parameters at 30°C and 40°C

Isotherms	Parameters	Values	
		30°C	40°C
Langmuir	Q_{max}(mgg^{-1})	56.75	85.83
Langmuir	b (L mg^{-1})	0.392	0.265
Langmuir	R_L	0.176	0.094
Langmuir	R^2	0.998	0.999
Freundlich	K_F(g mg^{-1} min$^{-1/n}$)	7.620	5.460
	1/n	0.472	0.351
	R^2	0.966	0.973
	b_T	227.358	536.684
Tempkin	a_T(L mg^{-1})	3.604	4.744
Tempkin	R^2	0.950	0.936
Tempkin	Q_s(mgg^{-1})	22.130	16.329
Dubinin-Radushkevich	β x 10^7 (mol J^{-1})^2	5.79	1.26
Dubinin-Radushkevich	E(kJ mol^{-1})	1.914	1.456
Dubinin-Radushkevich	R^2	0.994	0.997

4.0. CONCLUSION

Algae-mediated synthesis of metal oxide nanoparticles (MONPs) offers a promising and eco-friendly approach for addressing industrial challenges, like metal corrosion and wastewater pollution. The nanoparticles synthesized, using algal extracts rich in bioactive compounds, not only serve as effective corrosion inhibitors but also show strong adsorption capabilities for the removal of toxic dyes and heavy metals from simulated wastewater.

The unique composition of algae—containing proteins, polyphenols and polysaccharides—enables them to act as natural reducing, stabilizing and capping agents during nanoparticle synthesis, controlling particle size, shape, and surface properties.This green synthesis route is safer, more sustainable and less toxic compared to traditional chemical methods. It avoids harsh reagents, minimizes hazardous waste, and allows for large-scale production with enhanced nanoparticle stability. The synthesized MONPs form protective coatings on metal surfaces, reduce electrochemical reactions, and prevent biofilm formation, which are key mechanisms in corrosion resistance. In adsorption applications, the surface functionality and high reactivity of algal-based MONPs facilitate efficient pollutant removal from wastewater. While result impressive anti-corrosion efficiencies—often exceeding 90%, further studies needed for more corrosion protection applications from MONPs derived from the algae.

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IZVOD

SINTEZA NANOČESTICA NA BAZI METALA POMOĆU ALGI ZA ZAŠTITU OD KOROZIJE I ADSORPCIJU: PREGLED

Biosinteza nanočestica metalnih oksida (MONP) korišćenjem ekstrakata algi privukla je značajnu pažnju kao zelena i održiva strategija za zaštitu od korozije i sanaciju zasnovanu na adsorpciji. Metaboliti algi - posebno polisaharidi, proteini, fenoli i pigmenti - deluju kao prirodni agensi za redukciju, pokrivanje i stabilizaciju, nudeći obnovljivu alternativu toksičnim hemijskim metodama. Nedavni izveštaji ističu da razlike u vrstama algi (zelene, smeđe, crvene i cijanobakterije) značajno utiču na morfologiju, kristalnost i funkcionalnost površine nanočestica podvrgavanjem tehnikama karakterizacije; skenirajuća elektronska mikroskopija (SEM), rendgenski difraktometrija (XRD) i Furijeova transformaciona infracrvena spektroskopija (FT-IR), respektivno, što zauzvrat diktira njihove zaštitne i adsorptivne performanse. Napredak u sintetisanju ZnO, CuO i Fe_3O_4 *nanočestica putem ekstrakata algi pokazuje značajnu efikasnost inhibicije korozije (>90% u nekim kiselim i slanim sredinama) kroz mehanizme kao što su formiranje barijernog filma, otpornost na prenos naelektrisanja i pasivacija. Paralelne studije pokazuju visok kapacitet adsorpcije za teške metale (*Pb^{2+}, Cd^{2+}, Cr^{6+}*) i organske boje, što se pripisuje poroznosti nanočestica, modulaciji površinskog naelektrisanja i biološki izvedenim funkcionalnim grupama. Novi doprinosi iz novije literature naglašavaju dvostruku funkcionalnost ovih nanomaterijala, ističući ne samo njihovu otpornost na koroziju i efikasnost adsorpcije, već i njihovu podesivost kroz kontrolisane parametre sinteze kao što su pH, koncentracija prekursora i izbor vrsta algi. Zajedno, ovi uvidi pozicioniraju algama posredovane MONP kao obećavajuće kandidate za ekološki prihvatljive inovacije u nauci o materijalima u tehnologijama upravljanja korozijom i prečišćavanja otpadnih voda.*

Ključne reči: *Alge, Nanočestice metalnih oksida (MONP), Sinteza zelenih nanočestica, Ekološki prihvatljivi materijali, Zaštita od korozije, Adsorpcija, Premaz metalne površine.*

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