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Review article

GREEN CORROSION INHIBITORS FOR MILD STEEL: A COMPREHENSIVE REVIEW

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Abstract

Corrosion of mild steel is a significant challenge in various industrial sectors, leading to substantial economic and environmental costs. To address this issue various organic, inorganic, and mixed inhibitor have long been used. In recent years, there has been growing interest in the development of green and sustainable corrosion inhibitors to mitigate the adverse effects of corrosion. Nanomaterials have emerged as promising candidates for this purpose due to their unique properties and environmental friendly characteristics. Nanomaterials can act as effective barriers against corrosion by forming protective layers on the surface of mild steel. They can also inhibit electrochemical reactions that lead to corrosion, thus extending the lifespan of the material. This comprehensive review highlights the immense potential of nanomaterials as green corrosion inhibitors for mild steel, offering sustainable and eco-friendly solutions to combat corrosion related challenges. The integration of nanotechnology into corrosion inhibition strategies presents a promising path for the advancement of material sciences and the protection of mild steel in diverse industrial applications.

Keywords: Nanomaterial; Mild Steel; Corrosion Inhibitor; Green Synthesis.

Introduction

Corrosion, an inevitable natural process, poses significant challenges across industries, infrastructures, and environmental landscapes [1]. The continuous degradation of metallic structures, especially mild steel, due to corrosion inflicts substantial economic losses and environmental consequences globally [2]. This deterioration not only compromises the structural integrity of materials but also has a negative impact on ecosystems and human safety. The environmental impact stemming from corrosion is a multifaceted concern. The release of metal ions and rust byproducts into soil and water systems unfavorably affects biodiversity, water quality, and agricultural productivity [3]. To combat this issue, many organic and inorganic inhibitors are developed and used [4]. Their application is restricted due to the high cost as well as environmental and human toxicity [5,6]. To overcome these difficulties, a paradigm shift towards sustainable and environmental friendly corrosion inhibition strategies is necessary. The urgency to adopt green corrosion inhibitors has never been more pressing. These inhibitors not only mitigate corrosion but also align with the growing global consciousness towards eco-friendly practices, ensuring minimal environmental impact throughout their life cycle [7-10]. In this context, nanomaterials emerge as a promising avenue in the quest for green corrosion inhibitors. Their unique physiochemical properties, surface modifications, and tailored functionalities offer unusual opportunities to develop efficient, cost-effective, and environmental friendly solutions for corrosion protection [11]. This review paper aims to explore and evaluate the potential of nanomaterials as green corrosion inhibitors for mild steel. It provides a comprehensive understanding

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of nanomaterials as green corrosion inhibitors specifically tailored for safeguarding mild steel. By elucidating their synthesis, performance evaluation, and environmental implications, this comprehensive analysis seeks to make the path for sustainable corrosion mitigation strategies in a world increasingly conscious of environmental preservation.

Corrosion Processes in Mild Steel

Mild steel corrosion involves electrochemical reactions at the metal surface, leading to the degradation of the material [12]. Understanding this mechanism is crucial for the development and application of nanomaterial-based inhibitors. The corrosion process typically unfolds as follows [13].

Initiation Phase: Exposure of mild steel to environmental factors, notably moisture and oxygen, leads to the initiation of corrosion. Microscopic imperfections, such as surface defects or grain boundaries, serve as sites for the initial metal-corrosive agent interaction.

Anodic Reaction: At localized anodic sites, oxidation of iron on metal surface occurs to generate ferrous (Fe^{2+}) ions as per the reaction.

$$Fe \rightarrow Fe^{2+} + 2\,e^{-} \tag{1}$$

Cathodic Reaction: Simultaneously, oxygen and moisture in the environment are reduced at cathodic sites. Oxygen reduction can occur through various pathways, including-

Reduction of oxygen molecules (O_2) to hydroxide ions (OH^-):

$$O_2 + 2\,H_2O + 4\,e^{-} \rightarrow 4\,OH^{-} \tag{2}$$

Reduction of water (H_2O) to hydroxide ions:

$$2\,H_2O + 2e^{-} \rightarrow H_2 + 2\,OH^{-} \tag{3}$$

Formation of Iron Oxides (Rust): The generated ferrous ions combine with oxygen, resulting in various iron oxide products, commonly recognized as rust. The overall reaction involves the oxidation of iron and reduction of oxygen, leading to the formation of iron oxides:

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3 \tag{4}$$

Progression of Corrosion: The ongoing electrochemical reactions cause the accumulation of iron oxides, forming a porous and flaky rust layer on the steel surface. This layer resulted in continued corrosion, perpetuating the cycle.

Nanomaterials as Green Corrosion Inhibitors

Nanomaterials are extensively employed as next-generation corrosion inhibitors for metals and alloys in a range of electrolytes due to their exceptional physical and chemical properties and utilizing green synthesis techniques. Due to their distinct characteristics including high surface area, tailored surface chemistry, and controlled reactivity, they present an opportunity to intervene in these corrosion mechanisms [14-17]. They can function as inhibitors by adsorbing onto the metal surface, forming protective layers, altering the kinetics of electrochemical reactions, or hindering the transport of corrosive agents to the metal interface [18].

Types of Nanomaterials as Corrosion Inhibitor

Metal/Metal oxide Nanoparticles: Nanoparticles, characterized by their small size and large surface area, are often used as corrosion inhibitors. Metal nanoparticles such as silver, gold, zinc oxide, and cerium oxide exhibit excellent inhibitive properties as they form protective films on metal surfaces, hindering the corrosion process [19-23]. Additionally, semiconductor nanoparticles like titanium dioxide and zinc oxide nanoparticles have shown promise in mitigating corrosion through their photocatalytic activity [24,25]. A.M. Atta et. al. prepared a new magnetite nanoparticle coated with rosin amidoxime for mild steel inhibition in 1M HCl. They studied the corrosion protection properties of the prepared nanoparticle on steel by polarization and electrochemical impedance spectroscopy (EIS). The inhibition efficiency was found to be 96.8% with an inhibitor concentration of 150 ppm [26]. AgNPs from Kola nut were extracted by Asafa et. al. and investigated the inhibition efficiency on stainless steel, mild steel, and aluminium in 1M HCl solution. They studied their corrosion inhibition behaviour by using gravimetric, gasometric, and potentiodynamic polarization technique. The inhibition efficiency was found to be 99.59% for mild steel [27].

Nanocomposites: Nanocomposites are materials comprising a matrix reinforced with nanoscale particles or fibers. Incorporating nanoparticles into polymer matrices on metal coatings enhances their corrosion resistance. The synergistic effects of nanocomposites derive from combining the mechanical strength of the matrix material with the unique properties of nanoscale additives, forming robust barriers against corrosion [28]. Hany M. Abd El-Lateef et. al. synthesized polyaniline (PANI) and two modified loading of 5, 10 % Ti_2O_3-SiO_2/ PANI, in which Ti_2O_3-SiO_2 nanoparticles (NPs) were modified with PANI forming nanocomposites [29]. For the first time, E. A. Essien et al. experimented with olive-Ti nanocomposite made from ethanolic extract of olive leaves in TiCl4 solution. The synthesized nanocomposite efficiently prevented mild steel from corroding in acid, with an increase in inhibition efficacy from 83.5% to 93.4% after incorporation of Ti nanoparticles at a very low inhibitor concentration [30]. Chitosan-cobalt and chitosan-SnS_2 nanocomposites are synthesized using cobalt and tin sulphide nanoparticles by Monika Srivastava et.al. They utilized the nanocomposites to prevent corrosion of mild steel in 1 M HCl at ambient temperature. They found maximum corrosion inhibition efficiencies of CH-Co and CH-SnS_2 composite were 97% and 85%, which were clearly greater than alone chitosan (77%) [31].

Nanocontainers: A nanocontainer refers to a nanoscale structure or device designed to encapsulate and deliver substances at the molecular or nanoscale level. These nanocontainers have been explored for various applications, including drug delivery, catalysis, and sensing. When it comes to inhibitor storage, nanocontainers can be utilized as a means of encapsulating and protecting inhibitors from degradation or premature release. By entrapping inhibitors within the nanocontainer, their stability and activity can be preserved until they are released at the desired time and location. T. Chen et.al investigated some hollow mesoporous nanoparticles as nanocontainers for corrosion inhibition which proved to be promising [32]. A comparative study on the use of polyelectrolyte modified halloysite nanotubes (PHN), polyelectrolyte modified silica nanoparticles (PSN) and polyelectrolyte modified nanocapsules (PNC) was also carried out by Safaris et.al for encapsulating benzotriazole corrosion inhibitor [33].

Nanotubes and Nanowires: Carbon-based nanotubes and metallic nanowires possess exceptional mechanical strength and electrical conductivity, which can be harnessed for corrosion inhibition. Incorporating these nanomaterials into composites or coatings improves mechanical properties and provides pathways for controlled corrosion protection. Nanotubes, specifically carbon nanotubes (CNTs), have been investigated as potential corrosion inhibitors due to their unique properties and high surface area-to-volume ratio. Nanotubes can act as corrosion inhibitors as Barrier protection, Passivation, Ion adsorption, Self-healing coatings etc. Nanotubes form a passive layer on metal surface to fill the gap between metal- and polymer-based composite and it promotes sacrificial protection in polymer coatings; therefore, it functions as an anticorrosive filler. 50 nm diameter and 1000 nm length halloysite clay nanotubes were analyzed by Abdullayev et al as potential nanocontainers [34]. The nanotube loaded with benzotriazole can be mixed into paint to improve its anticorrosion property as well as the coating tensile strength. Benzotriazole release kinetics according to the time needed for the formation of a metal protective layer through copper complication. Halloysite nanotubes loaded with corrosion inhibitors like sodium diethyldithiocarbamate, green inhibitors like vanillin, thyme oil and a combination of both vanillin and thyme oil have been widely used to control corrosion in the oil and gas pipeline industries [35].

Green Synthesis Processes of Nanomaterials

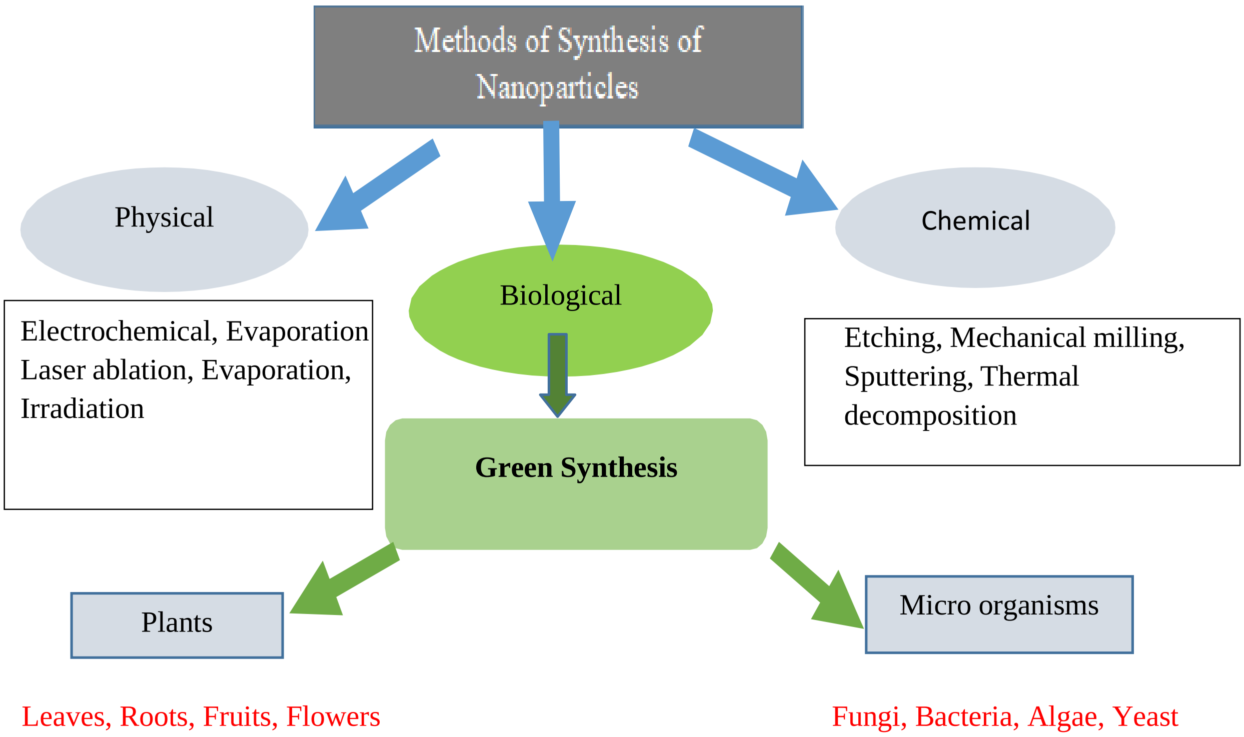

Fig. 1: Different methods of nanoparticle synthesis

Green synthesis of nanomaterials involves environmental friendly methods that utilize natural resources, sustainable materials, or eco-friendly approaches to produce nanoparticles. These methods (Fig 1) typically involve natural sources, such as plant extracts, microorganisms, or other bio-based materials, as reducing or capping agents to convert metal ions into nanoparticles. For the synthesis of metal/metal oxide nanoparticles, plant biodiversity has been broadly considered due to the availability of effective phytochemicals in various plant extracts, especially in leaves such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids [36]. These components are capable of reducing metal salts into metal nanoparticles. Here are several common techniques:

1. Plant-Mediated Synthesis

Extracts: Utilize extracts from plants (leaves, stems, fruits) rich in bioactive compounds that act as reducing and capping agents to convert metal ions into nanoparticles. Examples include neem, tea, aloe vera, Tulsi, curry leaves extracts, etc. [37-40]. The synthesis of metal nanoparticles using plant extracts is depicted in Fig 2 below.

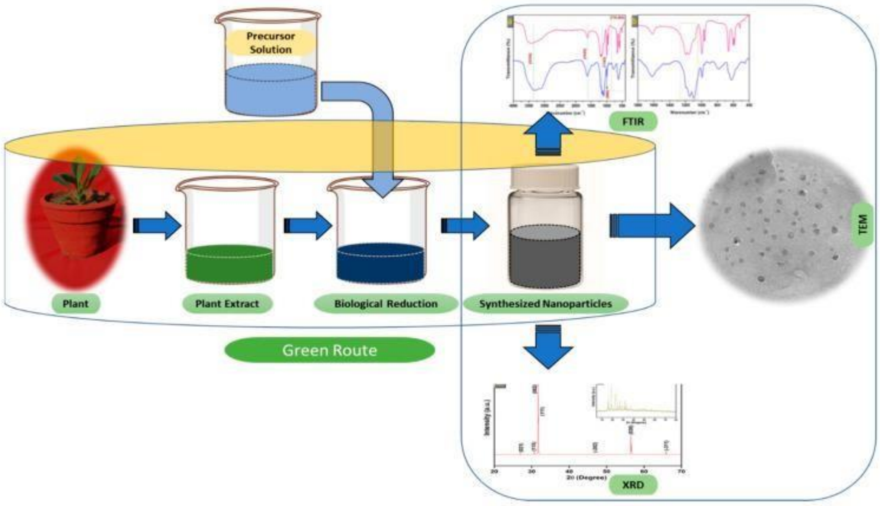

Fig. 2: Schematic of metal nanoparticle synthesis using plant extracts [40].

2. Microorganism and Bio-Based Synthesis

Bacteria, Fungi, Algae: Certain microorganisms possess enzymes, proteins, or metabolites capable of reducing metal ions, leading to the formation of nanoparticles. Microbial cells or their extracts are used in these processes [41]. Metal nanoparticles synthesis process using microorganism is depicted in Fig 3.
Polysaccharides and Proteins: Biomolecules like chitosan, starch, cellulose, or proteins derived from various sources also act as reducing and stabilizing agents to synthesize nanoparticles.

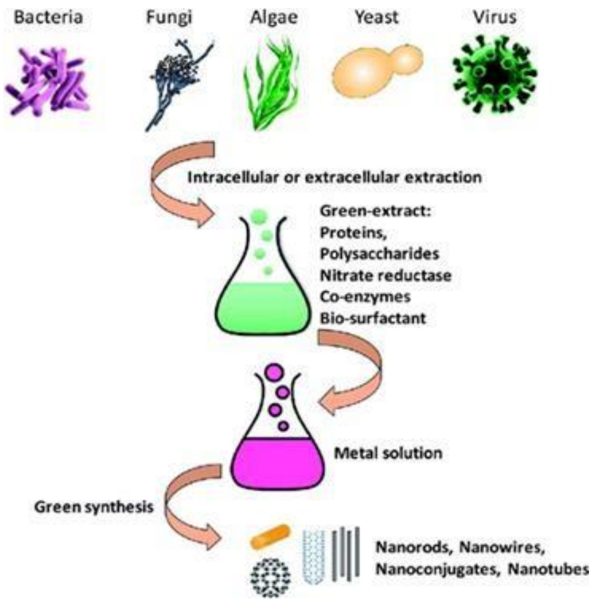

Fig. 3: Schematic of metal nanoparticle synthesis using microorganisms [41].

3. Microwave or Ultrasonic Irradiation

Application of microwave or ultrasonic energy accelerates the green synthesis process, reducing reaction times for nanoparticle formation. These methods are eco-friendly due to their energy efficiency.

4. Solar Irradiation

Utilizes sunlight to drive the synthesis of nanoparticles. Solar radiation acts as a catalyst in the reduction process, offering an environmentally friendly route.

5. Water as a Solvent

Employing water as a solvent in the synthesis process reduces reliance on toxic organic solvents, making the overall process more environmentally benign.

6. Green Precursors and Catalysts

Use of non-toxic, renewable precursors and catalysts in the synthesis process to minimize environmental impact. Green synthesis methods prioritize sustainability, minimize hazardous waste generation, and reduce the use of harmful chemicals. They often result in nanoparticles with excellent biocompatibility and potential applications in various fields.

Efficacy of Nanomaterials as Corrosion Inhibitors

A good inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production. Nanomaterials have shown promising efficacy as corrosion inhibitors due to their unique properties and interactions with metal surfaces. Research in this field has shown that nanomaterial based inhibitors exhibit enhanced corrosion protection compared to traditional methods. Various types of nanomaterials have been investigated and found to be good inhibitors with high inhibition efficiency. Comparison of some nanomaterials besed on their inhibition efficiency is tabulated below in Table 1.

Table 1: Comparison of different nanomaterials based on IC and % IE

Serial No	Inhibitor Name	Inhibitor Concentration (ppm)	% IE	References
1	Rosin Amidoxime/Magnetite nanoparticles	50	96.8	[19]
2	Ag NPs	6	91.6	[42]
3	GA-Ag NPs	1000	92.93	[43]
4	Linseed oil + IONPs	-	69.11	[44]
5	Olive oil + IONPs	-	80.88	[45]
6	CoO/Co_3O_4	80	89.8	[46]
7	Chitosan-CuO nanocomposite	-	96	[47]
8	Chitosan-SnS2 nanocomposite	400	84	[49]
9	Olive-Ti Nanocomposites	1000	93.4	[47]
10	HEI and Ag NPs	20	99	[48]

Conclusion

The exploration of nanomaterials as green corrosion inhibitors for mild steel presents a promising avenue toward sustainable and effective corrosion protection. The multifaceted nature of nanomaterials, coupled with their eco-friendly synthesis routes, underscores their potential significance in mitigating corrosion-induced damage in various industries and everyday applications. Through this comprehensive review, it becomes evident that nanomaterials offer a diverse range of mechanisms and functionalities that contribute to their effectiveness as corrosion inhibitors. Their high surface area, tailored properties, and synergistic effects with traditional inhibitors establish them as formidable contenders in corrosion prevention strategies. The synthesis methods explored in this review, utilizing plant extracts, microorganisms, and eco-friendly precursors, underscore the shift toward sustainable practices in material science. These methods not only reduce the environmental footprint but also yield nanoparticles with enhanced biocompatibility and reduced toxicity, aligning with the principles of green chemistry.

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Conflict of Interest

The authors declare no conflicting interests.

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