

BIOGENIC IRON OXIDE NANOPARTICLES AS INHIBITOR FOR CORROSION OF TMT ROD IN MARINE ENVIRONMENT

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ABSTRACT

This study involves the utilization of Iron Oxide and *Thespesia populnea* plant leaves as a protective coating for TMT rod surfaces in marine environments. Initially, the inhibitor was extracted from *Thespesia populnea* plant leaves using ethanol, and subsequently, Iron Oxide nanoparticles (FeNPs) were synthesized. Iron oxide nanoparticles were synthesized using a chemical precipitation process and their size effects were studied using Fourier transform infrared spectroscopy (FT-IR), Fourier ultraviolet-visible spectroscopy (UV-Visible), and scanning electron microscopy (SEM). Nanoparticle solutions were prepared and coated on the TMT rod and exposed to marine environment corrosion. At ten Coatings of FeNPs, the corrosion inhibition rate reached a maximum of 91.2% for 8mm rods, 95.4% for 10mm rods, and 98.7% for 16 mm rods respectively. The inhibition results showed that the FeNPs followed a physical adsorption process since they obeyed the Langmuir adsorption isotherm.

Keywords: Iron Oxide Nanoparticles; Biogenic Nanoparticle; Corrosion Inhibition; Marine Environment; Brackish Water.

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INTRODUCTION

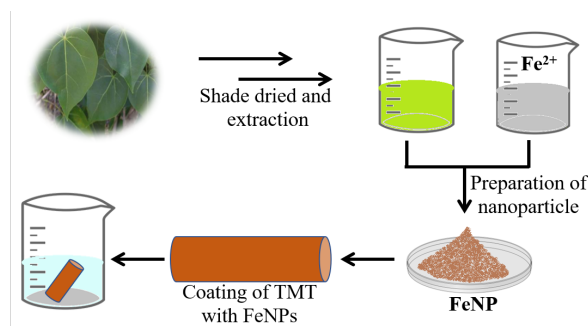
Metals deteriorate naturally by corrosion a natural process that happens when oxygen is present in the environment which causes reduction and oxidation.¹ Metals deteriorate through corrosion when they react with their surroundings. Corrosion is influenced by a variety of environmental factors including temperature, humidity, gases, salts, pollutants, salt concentrations, pH differences, and the types of electrolytes present on metal surfaces.²⁻¹⁰ Though corrosion is a natural process, it is controllable. A fifth of the world's steel production is produced to replace corrosion-related losses which amounts to about 4% of the global GDP.¹¹⁻¹⁵ despite the lack of detailed study to pinpoint the precise loss caused by different types of corrosion. Corrosion is estimated to cost India's economy between 4 and 6 percent of its GDP or more than Rs. 4,000 billion annually. Several methods exist for slowing down or preventing corrosion in metallic structures. The most common protective coatings used on metals include organic molecules, plastics, and polymers in addition to cathodic and/or anodized protection with organic or inorganic inhibitors. Chromium-based compounds are efficient preventive agents against corrosion. Yet toxicity issues are the main growing concerns. Utilizing inhibitors to stop corrosion on metal is a common choice. Inhibitors help to reduce corrosion by forming a protective coating on the metallic surface. In the metal sector, both chemical and natural inhibitors are widely utilized for preventing corrosion. Thermo Mechanically Treated steel (TMT) rod is a crucial structural component used in large buildings, water retention structures, ports, harbors, and bridges. TMT rods are susceptible to corrosion under unfavorable circumstances. There are a number of strategies to manage this including surface treatment, adding inhibitors to the concrete, and coating the concrete.^{3,4} In the majority of prior investigations organic compounds were evaluated for their capacity to shield steel from acid corrosion. Conifer cone extract for instance has been demonstrated to be able to stop steel rebar from corroding in a chloride-containing simulated concrete solution.¹⁶ Nanomaterials are effective in inhibiting corrosion because they have a much higher surface area per volume than traditional macro substances.¹⁵⁻²⁰ Because of their extremely

precise capacity to stop metal from corroding in a variety of environmental circumstances, nanoparticles could be used in industrial domains most significantly for this purpose. These materials hold immense promise for enhancing the performance and adaptability of various applications.²¹ A pivotal aspect of nanoscience involves the meticulous design of experimental procedures to craft nanoparticles with diverse chemical compositions, sizes, morphologies, and behaviors.²² Traditionally these nanoparticles have been synthesized through chemical or physical methods. However recent endeavors have seen a shift towards biological approaches for nanoparticle synthesis offering a range of benefits including safety, ecological friendliness, cost-effectiveness, and the elimination of harmful byproducts.^{23,24,25} Amongst the vast array of nanomaterials, nanoscale metals like iron have received considerable attention for their use in catalytic reactions, toxic waste treatment, highly efficient catalysts, and for use in the refractory metals sector.^{26,27} In parallel with these developments, green synthesis processes have emerged as a sustainable alternative for nanoparticle production. Green synthesis reduces pollution and fits with the concepts of waste reduction instead of remediation by using ecologically sound materials and harmless solvents like water and extracts from plants.^{28,29,30} This shift towards eco-conscious practices is particularly relevant today as environmental contamination poses significant threats to both human and animal health encompassing issues of toxicity, cancer risks, genetic mutations, and biodegradation.^{31,32} Additionally the unique properties of nanoparticles, stemming from their substantial surface area-to-volume ratio have been harnessed for various applications, including corrosion resistance enhancement.³⁵ Notably nanomaterials such as gold (Au), titanium dioxide (TiO₂), and copper oxide (CuO) have been explored to bolster corrosion resistance.^{26,35,36,37} Metal and their oxide nanoparticles are effective and useful at controlling corrosion. The biological production of nanoparticles is often proposed as a low-cost, environmentally acceptable solution to both physical and chemical methods. Plant-mediated nanoparticle synthesis is a green chemical strategy that combines nanotechnology and plants.^{33,34,38} In this perspective, the current study focuses on the analysis of iron oxide nanoparticles produced by *Thespesia populnea* (TP) leaf extract for preventing TMT rod corrosion in brackish water. The Indian tulip tree is an evergreen tree in the Malvaceae family. The plant is abundant in India's tropical and coastal forest areas. TP is readily accessible locally, relatively inexpensive, and environmentally friendly.

EXPERIMENTAL

Inhibitor Preparation

2 kg of fresh *Thespesia Populnea* (TP) leaves were collected at Nagapattinam District. The green leaves were allowed to dry for a two-week period under shade. The shade-dried TP leaves are powdered up and extracted using a Soxhlet method with 85% methanol (4 x 500 mL).^{11-13,27,38} The solution was subsequently passed through with the Whatman filtering paper. The resulting filtrate was then concentrated in a vacuum chamber to produce a material that resembled green oil and it was then kept in a refrigerator until it was used. The crude extract was colored green, orange-red, and yellow after being exposed to Fe³⁺, Mg-HCl, and NaOH respectively. Also when exposed to UV light, the crude extract displayed a purple spot and when exposed to ammonia, it became yellow. Moreover, the crude extract passed the Molisch's test indicating the presence of flavone glycoside (Scheme-1).



Scheme-1: Schematic Representation of Biogenic Synthesis of FeNPs and Inhibition of Corrosion of TMT Rod in Brackish Water

Preparation of FeNPs

100 mL of 0.01 M ferrous sulphate heptahydrate was prepared using a 70:30 water: ethanol mixture. After that 50 mL of 0.01 percent raw crude extract solution was added and it was thoroughly agitated. After allowing the reaction to run for three hours, another 50 mL of the 0.01 percent extract was included steadily drop by drop, and the resulting mixture was stirred for another 25 minutes. The particles are subsequently centrifuged, cleansed using double-distilled water, and then cleaned once more with ethanol. Thereafter the FeNPs were stored in ethanol until use after being dried in a vacuum for 24 hours at room temperature.

Characterization of FeNPs

The generated iron oxide nanoparticles have been characterized using an ultraviolet-visible spectrophotometer (JASCO, V-630) and an FT-IR spectroscopy (JASCO, FTIR-4100). Scanning electron microscopes and a dispersive energy spectrometer (SEM-EDS) were utilized to evaluate surface morphology and carry out analysis of elements (Hitachi S 3400N).

Weight Loss Measurements

The methods used to quantify weight loss were the same as those used in prior studies.^{7,18} In a nutshell, TMT rod of 3 different diameters, 8mm, 10mm, and 16mm, was abraded employing emery paper varying in grade from 600 to 1200. The rods were subsequently reduced in acetone and cleansed with distilled water. The 8 mm, 10 mm, and 16 mm rods were weighed separately and after which allowed to dry to ambient temperature. A solution of FeNP at 100 ppm was made. The inhibitor was then applied in coats of 1, 5, and 10 for the 8mm, 10mm, and 16mm TMT rods respectively. One coating of the TMT rod is thought to take 1 mL of 100 ppm FeNP. The 8 mm, 10 mm, and 16 mm rods were given 10 minutes to dry at room temperature following each coating. In this study, 8mm, 10mm, and 16mm TMT rod specimens with chemical makeups of C, 4.93%, magnesium, 1.09%, silica, and another Fe have been used.

Equations 1 and 2 were used to calculate inhibition efficiency (%IE), corrosion rate (CR), and surface coverage (θ).¹⁻²

$$IE(\%) = \frac{(W_2 - W_1)}{W_2} \times 100 \quad (1)$$

$$\theta = \frac{(W_2 - W_1)}{W_2} \quad (2)$$

Where W_1 is the weight of the specimen before incubation and W_2 is after incubation in the marine environment.

RESULTS AND DISCUSSION

The examination of crude extract and synthesized iron oxide nanoparticles (FeNPs) employed UV-visible spectroscopy, shedding light on their distinct spectral characteristics. In the UV-visible spectra of the crude extract two prominent bands were observed at approximately 279 nm and 324 nm indicative of the presence of flavones within the extract.¹¹⁻¹³ These absorbance peaks at specific wavelengths serve as evidence of the flavonoid content a class of compounds well-known for their diverse biological activities and potential health benefits. In contrast, the UV-visible spectrum of the FeNPs exhibited a unique absorption band at 219 nm this can be related to the nanoparticles' distinctive optical features. This distinctive band in the FeNPs spectrum underscores the successful synthesis of iron oxide nanoparticles with specific attributes signifying their potential utility in various applications. Furthermore the FT-IR (Fourier-transform infrared) spectra of FeNPs and crude extract provided valuable insights into their molecular compositions. In the FT-IR spectrum of the crude extract, discernible peaks were observed at wave numbers 3424 cm^{-1} , 3205 cm^{-1} , 1650 cm^{-1} , and 1384 cm^{-1} . These peaks matched the vibrations of a stretch of different functional groups, namely -O-H, -C-H, -C=O, and -C-O. These findings corroborate the presence of these specific chemical bonds within the crude extract aligning with the expected constituents of flavonoid-rich compounds.¹⁴⁻¹⁶ Conversely, the FT-IR spectrum of the FeNPs revealed

distinctive metal-oxygen interaction peaks at 597 cm^{-1} providing conclusive evidence of the iron oxide nanoparticles' unique chemical structure and confirming their successful synthesis. These spectral analyses not only validate the presence of key compounds in the crude extract but also elucidate the structural characteristics of the synthesized FeNPs, setting the stage for their potential applications in diverse fields.

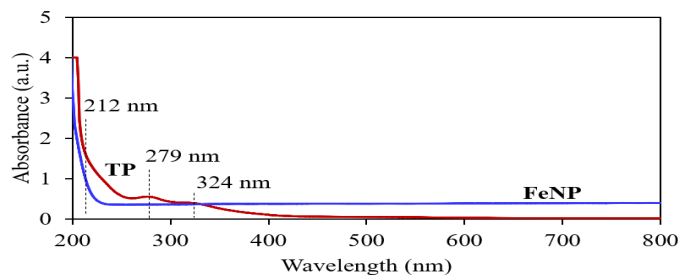


Fig.-1: UV-visible Spectra of TP and FeNP

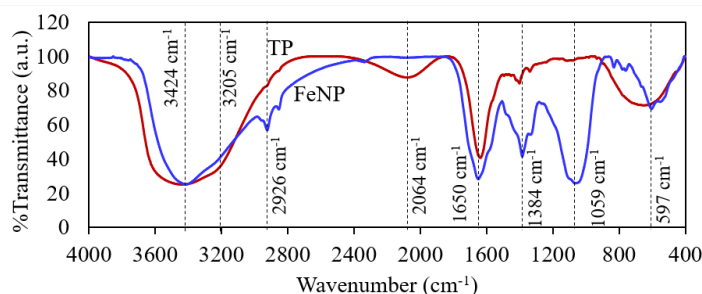


Fig.-2: FT-IR Spectra of TP and FeNP

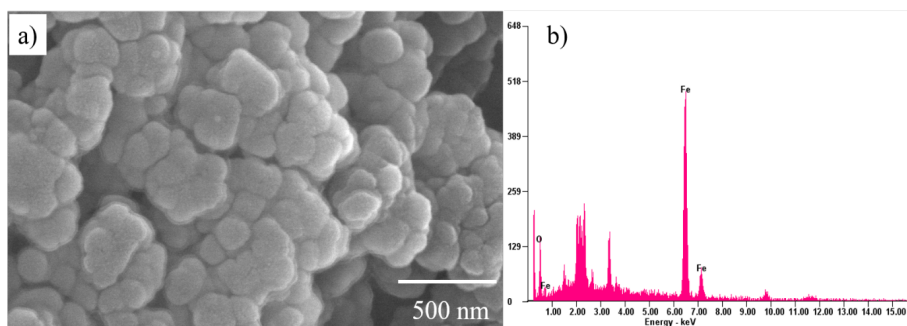


Fig.-3: (a) SEM Morphology and (b) EDS of FE Nanoparticles

Figure-3 displays the FeNPs morphologies. The FeNPs had an average diameter of $230 \pm 98\text{ nm}$. The SEM-ED spectrum was used to establish the nanoparticle's elemental composition which included 31.78% carbon, 25.2% oxygen, and 40.85% iron as the main constituents.

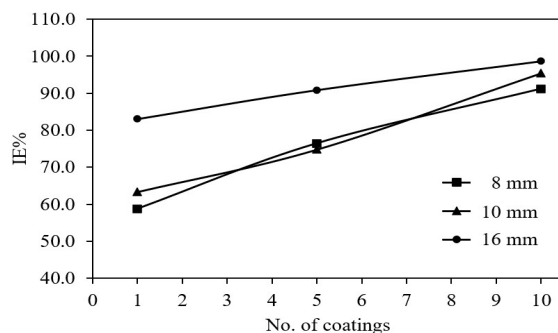


Fig.-4: Effect of Biogenic FeNPs on Corrosion Inhibition of TMT Rods in Brackish Water

Table-1: Corrosion Inhibition Effectiveness of Biogenic FeNPs and Thermochemical Parameters

Coating number	IE%	Surface Coverage(q)	Corrosion Rate (mm/y)	K (kJ/mol)	ΔG_{ads} (kJ/mol)
1	58.8	0.5882	0.8301	714	-16390
5	76.5	0.7647	1.0791	325	-14426
10	91.2	0.9118	1.2867	517	-15582

The 8 mm, 10 mm, and 16 mm TMT rod was coated with FeNPs in various numbers of coatings such as 1, 5, and 10 in order to assess the FeNPs effectiveness. The coated and uncoated TMT rods of 8mm, 10mm, and 16mm were both assessed in brackish water with a salinity of 5 ppt. Figure-4 illustrates how the number of FeNPs coatings seems to have an influence. The percentage of inhibition efficiency (%IE) and the number of FeNP coatings showed a linear relationship. For 8mm TMT rod inhibition efficacy was 58.8% for the first coating and subsequently improved to 76.5% at 5 coatings. An IE% of 91.2% was observed with 10 coatings on the TMT rod. The effectiveness of the FeNPs on 10 mm TMT rods was 63.4% for the first FeNPs coatings and increased to 74.8% after five FeNPs coatings. At ten FeNPs coatings, the effectiveness of the FeNPs in inhibition was observed to be 95.4%. For 16 mm TMT rod, the inhibition efficiency of FeNPs ranged from 83.4% for 1 coating and 90.9% after 5 coatings. The FeNP's efficiency in inhibiting was found to be 98.7% at 10 coatings. This is the result of molecules of FeNPs completely encasing the surface of the TMT rod. It is worth noting that as the diameter of the rod increases, so does the surface area and the inhibition efficacy of FeNPs increases as well. Further, on increasing FeNPs coatings, there was no vast improvement in %IE. The adsorption behavior of FeNPs can be used to gain insight into the process of corrosion inhibition. Figure-5 shows the adsorption isotherms. With correlation coefficient values of 0.9702 for 8mm TMT rods, 0.8599 for 10mm rods, and 0.9499 for 16mm rods, respectively, Fig.-5b demonstrates the nonlinear relationship between both the Temkin adsorption isotherm as well as weight loss data. Using correlation coefficient values of 0.9702 for 8mm TMT rod, 0.9874 for 10mm rod, and 0.9602 for 16mm rod the non-linear Freundlich adsorption isotherm correlation is displayed in Fig.-5c.

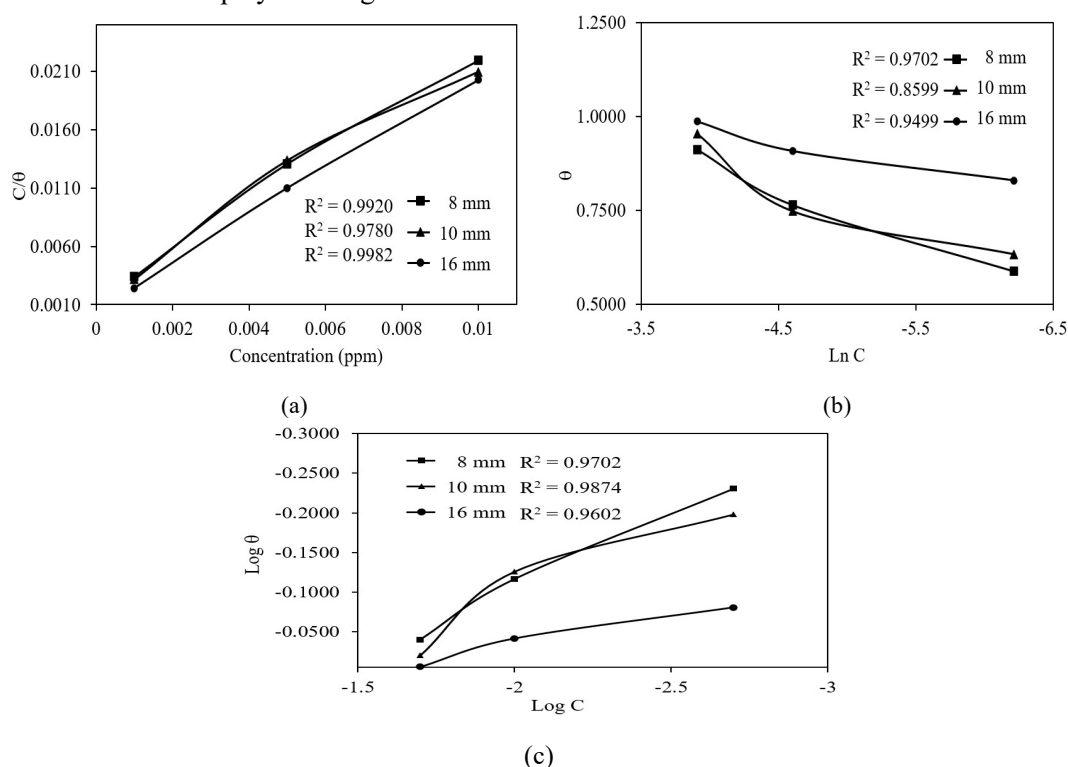


Fig.-5: (a) Langmuir, (b) Temkin and (c) Freundlich Adsorption Isotherms of Corrosion Inhibition of TMT Rod in Brackish Water using Biogenic FeNPs

With correlation coefficient values of 0.9922 for 16mm TMT rod, 0.9780 for an 8mm rod and 0.9920 for 10mm rod the Langmuir adsorption isotherm was more closely matched by FeNPs of TP. This is evident in Fig.-5a.

In light of this, the process of inhibition is probably an inhibitor's surface coverage by absorption upon the TMT surface.^{3,16,17} An increase in the inhibitor's inhibitive activity is likely due to the natural products' inclusion of heteroatoms and electrons as well as their bigger molecule size and more comprehensive coverage of the metallic surface. To determine the slopes and correlation coefficient, Langmuir adsorption isotherms were used. For the 8 mm, 10 mm, and 16 mm rods the slopes for the Langmuir adsorption isotherms were 2.0477, 1.9593, and 1.9786 respectively. Each nanoparticle detected in the inhibitor may have occupied multiple adsorption sites according to the results which showed that the value is greater than 1.0.

CONCLUSION

In light of the escalating concerns over the environmental impact and economic burden associated with corrosion, the quest for sustainable, cost-effective, and efficient corrosion inhibitors has intensified. This study delves into the realm of green inhibitors showcasing the remarkable potential of iron oxide nanoparticles (FeNPs) derived from *Thespesia Populnea* leaves. Our findings underscore several pivotal aspects that underscore the significance of this research. First and foremost the eco-friendliness and affordability of green inhibitors stand out as compelling attributes. In an era where environmental responsibility is paramount the utilization of FeNPs sourced from renewable *Thespesia Populnea* leaves aligns perfectly with sustainable practices. Moreover, the cost-effectiveness of this approach opens doors to widespread adoption, particularly in industries grappling with corrosion-related expenditures. Crucially our research elucidates the concentration-dependent efficacy of FeNPs as corrosion inhibitors. As the concentration of FeNPs increases the capacity to protect against corrosion offers a versatile tool for tailoring protection to specific requirements. This scalability is invaluable, particularly in the face of diverse and challenging corrosion scenarios. The adherence of *Thespesia Populnea* FeNPs to the Langmuir adsorption isotherm during adsorption provides critical insights into the molecular interactions underpinning corrosion inhibition. This knowledge enhances our understanding of the inhibitory mechanisms facilitating the design of even more effective corrosion protection strategies. Our study culminates in the visual and empirical confirmation of FeNP-based corrosion inhibition. Advanced microscopy techniques such as SEM and EDS offer tangible evidence supporting the efficacy of this corrosion protection method. These analyses underscore that corrosion protection occurs post-FeNP adsorption reaffirming the robustness of our findings. This research underscores the transformative potential of green-synthesized FeNPs from *Thespesia Populnea* leaves as a formidable solution in the ongoing battle against corrosion. Their eco-friendly nature, concentration-dependent efficacy adherence to the Langmuir adsorption isotherm, mixed-mode inhibition mechanism, and empirical validation through advanced microscopy collectively position them as a potent asset for safeguarding critical marine infrastructure. By extending the longevity and resilience of such infrastructure while promoting sustainable corrosion protection practices these FeNPs hold promise as a game changer in the corrosion protection landscape.

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CONFLICT OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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