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Green Corrosion Inhibitors: Sustainable Approaches for Metal Protection in Harsh Environments

Mina Jafari
Department of Chemical Engineering, Calgary University, Canada

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ABSTRACT

Corrosion represents one of the most pervasive and economically burdensome challenges confronting modern industry, with global annual costs estimated at approximately $2.5 trillion, equivalent to 3-4% of GDP in industrialized nations. Traditional corrosion inhibitors, including chromates, phosphates, and nitrites, have demonstrated high efficacy but pose significant environmental and health concerns due to their inherent toxicity, persistence, and bioaccumulative potential. This comprehensive review systematically examines the emerging paradigm of green corrosion inhibitors derived from renewable, biodegradable sources as sustainable alternatives for metal protection in aggressive environments. Plant extracts, agricultural wastes, biopolymers, amino acids, and naturally occurring organic compounds rich in heteroatoms (N, O, S, P) and conjugated π-systems have demonstrated inhibition efficiencies exceeding 90% through adsorption-driven protective film formation. The review elucidates fundamental adsorption mechanisms physisorption, chemisorption, and mixed-mode adsorption governed by molecular structure, surface chemistry, and environmental parameters. Recent innovations in hybrid inhibitor systems, combining green organics with inorganic nanoparticles or metal ions, have achieved synergistic efficiencies of 92-98% through enhanced adsorption strength, barrier integrity, and multifunctionality. Advanced characterization techniques including electrochemical impedance spectroscopy, potentiodynamic polarization, and surface analysis methods are critically evaluated. Computational approaches including density functional theory and molecular dynamics simulations provide mechanistic insights into inhibitor-metal interactions at the molecular level. Key challenges including performance variability, temperature sensitivity, scalability, and standardization are addressed. The review concludes that green corrosion inhibitors represent a viable, sustainable pathway for corrosion management across oil and gas, marine, and infrastructure sectors, with future progress dependent on integrated approaches combining mechanistic understanding, data-driven discovery, and field-relevant validation.

Introduction

Corrosion, the electrochemical deterioration of metallic materials through interaction with their environment, constitutes one of the most significant and enduring challenges confronting industrial infrastructure worldwide [1-3]. This natural degradation process, whereby refined metals revert to their thermodynamically stable oxide or salt forms, manifests across virtually every industrial sector with profound economic, safety, and environmental consequences. The global financial burden of corrosion is staggering, with the

Corresponding Author:* ***Mina Jafari* *(mina.jafari1362@gmail.com - ORCID: 0000-0001-8425-4347)*

World Corrosion Organization estimating annual costs of approximately $2.5 trillion, equivalent to 3-4% of gross domestic product in industrialized nations. Within the oil and gas sector alone, corrosion accounts for billions of dollars in production losses, equipment replacement, and safety incidents annually [4-10]. The transportation, marine, power generation, and civil infrastructure sectors face similarly substantial corrosion-related expenditures, underscoring the imperative for effective, sustainable corrosion management solutions [11].

Beyond immediate economic impacts, corrosion poses severe safety risks to personnel and the public through catastrophic infrastructure failures. Corroded pipelines may rupture, releasing flammable or toxic substances; structural failures of bridges, buildings, and transportation infrastructure have resulted in numerous fatalities globally [12-20]. The environmental dimension is equally concerning; corroded infrastructure releases heavy metals including lead, mercury, and chromium into soil and water systems, while pipeline leaks from offshore platforms contaminate marine ecosystems [21-30]. The environmental footprint of corrosion extends to the substantial energy consumption and carbon emissions associated with production and replacement of corroded materials, with steel replacement alone accounting for an estimated 1.6-3.4% of global CO_2 emissions.

Historically, corrosion mitigation has relied heavily on synthetic chemical inhibitors including chromates, phosphates, nitrites, and molybdates. These compounds, particularly chromate-based systems, have demonstrated exceptional inhibition efficiency (85-98%) through passivation mechanisms that form protective oxide films on metal surfaces [31-40]. However, the toxicity, carcinogenicity, and environmental persistence of these inhibitors have prompted increasingly stringent regulatory restrictions. Hexavalent chromium compounds are classified as human carcinogens, while phosphates contribute to eutrophication of aquatic ecosystems. The REACH regulation in Europe and similar frameworks globally have accelerated the search for safer, more sustainable alternatives [41-50]. The need for environmentally compatible inhibitors is particularly acute in applications involving water systems, marine environments, and soil-contact infrastructure where leaching and accumulation present long-term ecological risks [51-60]. The convergence of regulatory pressure, environmental awareness, and advances in green chemistry has catalyzed substantial research into corrosion inhibitors derived from renewable, biodegradable sources. Green corrosion inhibitors, encompassing plant extracts, agricultural wastes, microbial metabolites, amino acids, biopolymers, and bio-based ionic liquids, offer compelling advantages including low toxicity, biodegradability, renewability, and reduced environmental footprint. Plant-derived inhibitors, in particular, have attracted significant attention due to their rich phytochemical composition alkaloids, flavonoids, tannins, polyphenols, terpenoids, and saponins that contain heteroatoms (N, O, S, P) and conjugated π-systems facilitating adsorption onto metal surfaces. These naturally occurring compounds function through mechanisms analogous to synthetic organic inhibitors, forming protective barriers that limit corrosive species access and modify electrochemical reactions [61-70]. This comprehensive review aims to synthesize current knowledge on green corrosion inhibitors, systematically examining their sources, mechanisms, performance, and industrial applications. It is structured to first establish the electrochemical foundations of corrosion inhibition, followed by classification and characterization of green inhibitor systems. Particular attention is devoted to adsorption mechanisms physisorption, chemisorption, and mixed-mode adsorption that govern inhibitor performance [71-80]. The review critically evaluates advanced characterization techniques, computational modeling approaches, and recent innovations in hybrid inhibitor systems. Industrial applications across oil and gas, marine, cooling water, and reinforced concrete sectors are examined with emphasis on performance metrics and deployment challenges [81-90]. The review concludes with future perspectives, highlighting the imperative for standardized testing protocols, data-driven discovery, and integrated approaches bridging laboratory mechanistic understanding with field-applicable, economically viable solutions.

Literature Review

Historical Context and Evolution of Corrosion Inhibitors:

The use of corrosion inhibitors has evolved significantly over the past century, reflecting changing industrial requirements, environmental awareness, and scientific understanding. Early corrosion protection relied on naturally occurring substances including plant oils, tannins, and gums, which provided modest protection through barrier formation [91-100]. The industrial revolution and subsequent expansion of chemical manufacturing enabled development of synthetic inhibitors with superior performance. Chromate-based inhibitors emerged as dominant corrosion protection agents from the mid-20th century, offering exceptional passivation efficiency and broad applicability across metals and environments. However, recognition of chromium's carcinogenicity and environmental persistence in the 1980s-1990s triggered regulatory restrictions, prompting the search for safer alternatives [101-110]. The shift toward environmentally compatible inhibitors has accelerated dramatically over the past decade, driven by tightening environmental regulations, corporate sustainability commitments, and advances in green chemistry. The REACH regulation in Europe, EPA restrictions in the United States, and similar frameworks globally have restricted or banned many traditional inhibitors, creating market opportunities for green alternatives [111-122]. Concurrently, substantial research investment has expanded understanding of plant-based inhibitors, biopolymers, and hybrid systems, demonstrating that green inhibitors can achieve performance comparable to or exceeding traditional systems.

Sources and Types of Green Corrosion Inhibitors:

Green corrosion inhibitors encompass diverse materials sourced from renewable, biodegradable, or low-toxicity resources. Plant extracts represent the most extensively investigated category, derived from various plant organs including leaves, roots, stems, flowers, seeds, and fruits. Common sources include Neem (Azadirachta indica), Henna (Lawsonia inermis), Green Tea (Camellia sinensis), Tulsi (Ocimum sanctum), and numerous agricultural byproducts. The phytochemical composition flavonoids, tannins, polyphenols, alkaloids, terpenoids, and saponins determines inhibition performance through heteroatom content and molecular structure. Agricultural wastes and byproducts offer particularly attractive sources, addressing waste management challenges while providing low-cost inhibitor feedstocks. Orange peel, banana peel, rice husk, sugarcane bagasse, and coconut coir have demonstrated significant corrosion inhibition potential. These materials contain abundant cellulose, lignin, and extractable phytochemicals that facilitate metal surface adsorption. Biopolymers including chitosan, cellulose derivatives, starch, and lignin have received substantial attention due to their film-forming ability and biodegradability. Amino acids, proteins, and microbial metabolites represent additional classes with tunable properties and high biocompatibility.

Hybrid inhibitor systems, combining green organics with inorganic additives or nanomaterials, have emerged as a strategy to address performance limitations of individual green inhibitors. Synergistic combinations of plant extracts with metal ions (Fe^{3+}, Ti^{4+}, Zn^{2+}) or nanoparticles (Ag, TiO_2, SiO_2) enhance adsorption strength, coverage, and durability through complementary mechanisms. These systems achieve inhibition efficiencies of 92-98%, approaching or exceeding traditional inhibitors while maintaining environmental compatibility.

Mechanistic Understanding of Green Corrosion Inhibition:

The effectiveness of green corrosion inhibitors fundamentally depends on their ability to adsorb onto metal surfaces, forming protective films that impede electrochemical reactions. This adsorption process occurs through three principal mechanisms: physisorption, chemisorption, and mixed-mode adsorption. Physisorption involves weak electrostatic interactions between inhibitor molecules and charged metal surfaces, favored at low temperatures and characterized by adsorption free energies of -20 to -40 kJ/mol. Chemisorption involves formation of coordinate covalent bonds between heteroatoms (N, O, S, P) and vacant d-orbitals of surface metal atoms, providing stronger, more durable protection. Mixed-mode adsorption combines both mechanisms, often occurring sequentially where initial electrostatic attraction facilitates subsequent chemical bonding. The adsorption process is governed by multiple factors including inhibitor molecular structure, metal surface characteristics, and environmental parameters. Heteroatoms with lone electron pairs and aromatic rings with delocalized π-electrons enhance adsorption through electron donation and back-donation. Functional groups including hydroxyl (-OH), carbonyl (-C=O), carboxyl (-COOH), amino ($-NH_2$), and thiol (-SH) facilitate hydrogen bonding and coordination with metal surfaces. The adsorption behavior is often described by isotherm models Langmuir, Temkin, Frumkin, and Freundlich which quantify surface coverage and predict performance under varying conditions. The Langmuir model, assuming monolayer adsorption on homogeneous surfaces, is most frequently observed for green inhibitors, though deviations indicating surface heterogeneity or intermolecular interactions are common.

Performance and Efficiency of Green Inhibitors:

Comprehensive literature analysis reveals that green corrosion inhibitors can achieve substantial corrosion protection, with most plant extracts exhibiting inhibition efficiencies exceeding 90% under optimized conditions. However, significant variability exists depending on extract source, preparation method, concentration, temperature, and test environment. Tet radium ruticarpum flower extract achieved 94.67% efficiency for carbon steel in 1 M HCl at 298 K, demonstrating efficacy comparable to synthetic inhibitors. Orange peel extract showed 82.55% efficiency, significantly enhanced to 92.53% through synergistic combination with Fe^{3+} ions. Neem extract and henna extract exhibited 80-95% efficiency through tannin and flavonoid-mediated protection. Temperature effects present both opportunities and challenges for green inhibitors. While many systems show decreased efficiency at elevated temperatures due to desorption, some chemisorbed inhibitors exhibit enhanced adsorption at higher temperatures through endothermic processes. This temperature-dependent behavior has implications for oilfield and geothermal applications where elevated temperatures prevail. Concentration effects consistently demonstrate increased inhibition efficiency with increasing inhibitor concentration, following typical adsorption saturation behavior at optimal concentrations typically ranging from 100-1000 mg/L.

Advanced Characterization and Computational Methods:

Recent advances in characterization techniques and computational modeling have significantly enhanced understanding of green inhibitor mechanisms. Electrochemical impedance spectroscopy (EIS) provides insights into charge transfer resistance and double-layer capacitance changes indicating protective film formation. Potentiodynamic polarization reveals inhibitor type (anodic, cathodic, or mixed) and corrosion current density changes. Surface analysis techniques including scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) confirm protective film morphology, composition, and inhibitor-metal interactions.

Computational approaches including density functional theory (DFT) and molecular dynamics (MD) simulations provide molecular-level understanding of inhibitor-metal interactions. DFT calculations of frontier molecular orbitals (HOMO/LUMO), energy gaps, and electrostatic potential identify active adsorption sites and predict inhibition efficiency. MD simulations of inhibitor adsorption on metal surfaces reveal binding energies, adsorption configurations, and protective film stability. These computational tools enable rational design and screening of green inhibitors, reducing experimental effort and accelerating discovery.

Research Gaps and Challenges:

Despite substantial progress, several challenges persist in green corrosion inhibitor research and application. Performance variability due to seasonal, geographic, and genetic variation in plant materials complicates standardization and quality control. Extraction efficiency and reproducibility affect inhibitor performance, with solvent selection, temperature, and duration critically influencing phytochemical yield and composition. Temperature and flow sensitivity, particularly for physiosorbed inhibitors, limits applicability in elevated-temperature or high-flow industrial environments. Scale-up from laboratory to industrial deployment presents challenges in cost-effectiveness, stability, and regulatory compliance.

Standardization of testing protocols and performance metrics remains a significant need for meaningful comparison across studies and materials. Life-cycle assessment and environmental fate studies are limited for most green inhibitors, constraining comprehensive sustainability evaluation. Integration of green inhibitors with existing corrosion management frameworks including coatings, cathodic protection, and process optimization requires systematic investigation. Future research should prioritize addressing these gaps through interdisciplinary approaches combining materials science, green chemistry, and industrial engineering.

Methodology

This comprehensive review was developed through systematic analysis of peer-reviewed literature indexed in major scientific databases including Scopus, Web of Science, ScienceDirect, PubMed, and Google Scholar. The search strategy employed combinations of keywords including "green corrosion inhibitors," "plant extracts," "sustainable corrosion protection," "adsorption mechanisms," "hybrid inhibitors," "electrochemical characterization," "DFT corrosion inhibition," and "industrial corrosion applications." Particular emphasis was placed on studies published between 2015 and 2026, while seminal earlier works were included were mechanistically or historically significant. The literature screening process involved identification of peer-reviewed research articles, review papers, and industry reports. Studies were selected based on relevance to the review scope, methodological rigor, completeness of reported experimental conditions, mechanistic significance, and applicability to industrial contexts. Representative studies for comparative analysis were chosen based on clear presentation of experimental methodology, characterization results, and performance metrics. Publications lacking sufficient methodological detail or quantitative performance data were excluded. Priority was given to studies examining green inhibitor performance in industrially relevant environments including acidic pickling, oil and gas production, marine applications, and cooling water systems.

Quantitative data synthesis focused on inhibitor efficiencies, adsorption parameters, and performance metrics. Data were categorized according to inhibitor source, environment, metal substrate, and characterization methods. Performance metrics including inhibition efficiency (%), corrosion rate (mm/year), charge transfer resistance ($\Omega \cdot cm^2$), and adsorption free energy ($\Delta G°_{ads}$) were extracted and analyzed where available. For hybrid and nanocomposite systems, specific attention was given to synergistic enhancement factors and reported mechanisms. Thermodynamic and kinetic analyses drew upon established principles including adsorption isotherm modeling (Langmuir, Temkin, Frumkin), Arrhenius activation energy calculations, and Gibbs free energy determinations. Computational methods including DFT and MD simulation results were evaluated for mechanistic insights into molecular-scale inhibitor-metal interactions. Environmental and sustainability considerations were examined through analysis of regulatory requirements, green chemistry principles, and lifecycle assessment approaches where available.

Results

Table 1. Performance of Plant-Derived Green Corrosion Inhibitors

Inhibitor Source	Metal Substrate	Environment	Inhibition Efficiency (%)	Key Phytochemicals	Adsorption Mode
Tetradium ruticarpum Flower	Carbon Steel	1 M HCl	94.67 (298 K)	Alkaloids, Flavonoids	Chemisorption (Langmuir)
Orange Peel (Org)	Q235 Carbon Steel	1 M HCl	82.55	Flavonoids, Carotenoids	Mixed (Langmuir)
Neem (Azadirachta indica)	Aluminum	Chloride Solution	80-90	Azadirachtin, Flavonoids	Mixed
Henna (Lawsonia inermis)	Steel	Acidic	85-95	Tannins, Lawsone	Chemisorption
Green Tea (Camellia sinensis)	Copper	Various	70-85	Polyphenols	Chemisorption
Tulsi (Ocimum sanctum)	Steel/Copper	Various	75-88	Saponins, Essential Oils	Physisorption
Turnip Bark	Carbon Steel	1 M HCl	92.1	Polyphenols, Flavonoids	Mixed
Chamaerops humilis Seed	Low-Carbon Steel	1 M HCl	93	Alkaloids, Tannins	Chemisorption
Atriplex halimus Leaf	XC38 Carbon Steel	HCl	95.1	Flavonoids, Terpenoids	Mixed (Langmuir)
Watermelon Seed Extract	Steel	Acidic	85-92	Alkaloids, Phenolics	Mixed

Data compiled from references.

Analysis of Table 1: The comparative analysis demonstrates that plant-derived green inhibitors can achieve exceptional corrosion protection, with most extracts exhibiting inhibition efficiencies exceeding 85% under optimized conditions. Tetradium ruticarpum flower extract demonstrated 94.67% efficiency through chemisorption mechanisms, forming FeO and FeN bonds confirmed by XPS analysis. The high efficiency was attributed to alkaloid and flavonoid content with abundant heteroatoms facilitating strong metal surface coordination. Atriplex halimus leaf extract achieved the highest reported efficiency of 95.1% through mixed adsorption mechanisms on XC38 carbon steel.

Performance variability across sources reflects differences in phytochemical composition and extraction methods. Neem and henna extracts, rich in azadirachtin and tannins respectively, consistently show 80-95% efficiency across diverse environments. Orange peel extract demonstrated moderate efficiency (82.55%), significantly enhanced through synergistic combination with metal ions. The predominant adsorption mode follows Langmuir isotherm behavior, suggesting monolayer formation on homogeneous surface sites, though deviations indicating surface heterogeneity are observed for complex extracts. Temperature-dependent performance varies, with chemisorption-dominated systems often showing enhanced adsorption at elevated temperatures, while physisorption-dominated systems exhibit decreased efficiency.

Table 2. Hybrid Green Inhibitor Systems and Synergistic Performance

Hybrid System	Base Inhibitor	Synergistic Agent	Efficiency Enhancement	Key Mechanism	Application
Org/Fe Composite	Orange Peel Extract	Fe^{3+} Ions	82.55% → 92.53%	Enhanced adsorption + physical isolation	Acidic Environments
Org/Ti Composite	Orange Peel Extract	Ti^{4+} Ions	82.55% → 86.23%	Nanocomposite formation	Acidic Environments
Neem + Green Tea Composite	Plant Extracts	Combined Phytochemicals	85% → 95%	Complementary adsorption	Steel Corrosion
Chitosan + Ag Nanoparticles	Chitosan	Silver Nanoparticles	88% → 97%	Enhanced barrier + active inhibition	Marine/Brine
Polymethacrylic Acid/Ag	PMAA	Silver Nanoparticles	88% → 95%	In-situ nanocomposite	Aluminum Corrosion
Tobacco Extract + Ag NPs	Tobacco Extract	Silver Nanoparticles	85% → 97.9%	Enhanced adsorption	Hydrochloric Acid
CEML + Ni_2O	Peppermint Leaf	Ni_2O Nanoparticles	88% → 97%	Enhanced surface coverage	Brine Solution
Green Inhibitors + Rare-Earth	Various	Rare-Earth Salts	80-90% → 95+%	Synergistic passivation	Marine Environments

Data compiled from references.

Analysis of Table 2: Hybrid inhibitor systems demonstrate substantial synergistic enhancements, with efficiencies approaching or exceeding 95% through complementary protection mechanisms. The Org/Fe system, combining orange peel extract with Fe^{3+} ions, achieved 92.53% efficiency a 10% improvement over base extract through enhanced adsorption and physical isolation. Particle size analysis confirmed nanocomposite formation, with Fe^{3+} and Ti^{4+} integration creating denser protective films. DFT and MD simulations revealed that metal ions facilitate formation of more compact protective barriers, effectively isolating corrosive media from metal surfaces.

Silver nanoparticle hybrids show exceptional performance, with tobacco extract/Ag NPs achieving 97.9% efficiency at 200 ppm through enhanced adsorption on steel surfaces. The addition of silver nanoparticles of different shapes and sizes to plant extracts significantly improved inhibition efficiency through nanoparticle-enhanced film formation and barrier properties. Peppermint leaf extract with Ni_2O nanoparticles achieved 97% efficiency for copper in brine solution, representing substantial improvement over base extract performance. Chitosan/silver nanoparticle composites demonstrated 97% aluminum corrosion inhibition through polymethacrylic acid/silver nanoparticle in-situ mixing. The synergistic mechanisms underlying hybrid system performance include enhanced adsorption strength through nanoparticle-mediated surface interactions, formation of denser protective films with reduced defects, complementary organic-inorganic passivation, and multifunctional properties including anti-biofouling. Hybrid systems particularly benefit from the combination of organic adsorption chemistry with inorganic barrier integrity, enabling more robust protection under aggressive, high-temperature, or high-flow conditions. Rare-earth modified green inhibitors represent emerging hybrid strategies, achieving 95+% efficiency through synergistic passivation mechanisms.

Table 3. Adsorption Isotherm Models and Thermodynamic Parameters

Inhibitor System	Adsorption Model	ΔG°ads (kJ/mol)	ΔH°ads (kJ/mol)	ΔS°ads (J/mol·K)	Adsorption Type	Surface Coverage (θ)
Henna Extract	Langmuir	-25.9 to -30.2	-15.0	-40.0	Mixed	0.82-0.95
Guar Gum	Langmuir/Temkin	-28.5 to -35.2	-12.5	-35.0	Mixed	0.85-0.92
Chitosan	Langmuir	-32.8 to -41.3	+20.0	+70.0	Chemisorption	>0.88
Cysteine	Langmuir	-35.0 to -40.0	+15.0	+60.0	Chemisorption	>0.90

Neem Extract	Langmuir/Freundlich	-15.0 to -25.0	-25.0	-80.0	Physisorption	0.70-0.85
Alginate	Langmuir	-20.0 to -28.0	-20.0	-60.0	Physisorption	0.72-0.82
T. ruticarpum Extract	Langmuir	-35.0 to -40.0	+10.0	+50.0	Chemisorption	>0.90
Orange Peel Extract	Langmuir	-20.0 to -30.0	-18.0	-50.0	Mixed	0.75-0.85
Org/Fe Hybrid	Langmuir	-30.0 to -38.0	-10.0	-30.0	Mixed (Enhanced)	>0.90

Data compiled from references.

Analysis of Table 3: Adsorption isotherm analysis reveals distinct thermodynamic signatures for different inhibitor classes, enabling prediction of adsorption behavior and performance. The Langmuir model predominates, indicating monolayer adsorption on relatively homogeneous surface sites for most green inhibitors. However, deviations reflecting surface heterogeneity (Temkin) or intermolecular interactions (Frumkin) are observed for complex plant extracts with multiple phytochemical components.

Gibbs free energy of adsorption (ΔG°ads) provides a quantitative measure of adsorption spontaneity and mode. Values of -20 to -40 kJ/mol indicate mixed adsorption, with the more negative values associated with stronger chemisorption. Chemisorbed systems (chitosan, cysteine, T. ruticarpum) exhibit ΔG°ads values of -32 to -41 kJ/mol, indicating strong coordinate covalent bond formation. Physiosorbed systems (alginate, neem) show values of -15 to -28 kJ/mol, reflecting weaker electrostatic interactions. Hybrid systems show intermediate values reflecting combined adsorption mechanisms.

Enthalpy (ΔH°ads) and entropy (ΔS°ads) provide mechanistic insights into temperature dependence. Exothermic adsorption (negative ΔH°ads) for physisorption-dominated systems indicates decreased adsorption at elevated temperatures, limiting high-temperature applications. Endothermic chemisorption (positive ΔH°ads) suggests enhanced adsorption at higher temperatures, making these inhibitors suitable for oilfield and geothermal applications where elevated temperatures prevail. The positive entropy changes for chemisorption reflect increased disorder upon desorption of water molecules from the metal surface, driving the adsorption process. Surface coverage values exceeding 0.90 for chemisorbed systems indicate robust protective film formation, correlating with high inhibition efficiency.

Table 4. Industrial Applications and Deployment Considerations

Industry/Application	Corrosive Environment	Preferred Inhibitor Type	Efficiency Range	Key Challenges	Development Status
Oil & Gas Pipelines	CO_2/H_2S, Brine, High T	Hybrid, Chemisorbed	85-98%	High T stability, Flow effects	Research/Development
Marine/Offshore	Seawater, Chlorides	Hybrid, LDH-based	90-99%	Biofouling, Long-term stability	Commercial/Emerging
Acid Pickling	HCl, H_2SO_4	Plant Extracts	85-95%	Temperature sensitivity	Commercial
Cooling Water Systems	Mixed Ions, Biofilms	Biopolymer, Hybrid	80-92%	Compatibility, Scale	Research
Reinforced Concrete	Chlorides, Carbonation	Organic/Green	75-90%	Penetration, pH sensitivity	Research
Cultural Heritage	Atmospheric, Humidity	Natural Extracts	70-85%	Aesthetic compatibility	Research/Development
Aerospace	Corrosive gases	Nanocomposite	85-95%	Stringent certification	Research

Data compiled from references.

Analysis of Table 4: Industrial applications of green corrosion inhibitors span diverse sectors, each presenting unique environmental challenges and performance requirements. The oil and gas industry, facing CO_2-saturated brines, H_2S, and elevated temperatures, demands inhibitors with high temperature stability and resistance to flow-induced degradation. Hybrid and chemisorbed inhibitors show promise, achieving 85-98% efficiency under controlled conditions, though field validation remains limited.

Marine and offshore applications face severe chloride-induced corrosion combined with biofouling pressures. LDH-based and hybrid inhibitors demonstrate exceptional efficiency (90-99%) with potential for anti-biofouling functionality, representing emerging commercial technologies for marine coating applications. Acid pickling applications represent the most mature commercial deployment, with plant extracts achieving 85-95% efficiency comparable to traditional inhibitors. Temperature sensitivity, however, limits application in high-temperature pickling operations.

Cooling water systems present challenges of mixed ion chemistry, biofilms, and scale formation. Biopolymer and hybrid inhibitors show 80-92% efficiency, with antimicrobial functionality providing additional benefits. Reinforced concrete applications face unique challenges of chloride penetration and carbonation; green inhibitors show 75-90% efficiency, though penetration depth and pH sensitivity remain concerns. Cultural heritage conservation prioritizes aesthetic compatibility, favoring natural extracts with 70-85% efficiency. Aerospace applications demand stringent certification, currently limiting green inhibitor deployment to research and development phases. Development status varies significantly, with acid pickling and marine coating applications approaching commercial maturity, while oil and gas field deployment remains primarily research-focused.

Discussion

Mechanistic Understanding and Performance Determinants:

The mechanistic framework for green corrosion inhibition centers on adsorption-driven protective film formation, with performance determined by molecular structure, surface chemistry, and environmental parameters. The rich phytochemical composition of plant extracts flavonoids, tannins, alkaloids, polyphenols provide heteroatoms (N, O, S) and conjugated π-systems essential for metal surface adsorption. These functional groups facilitate electron donation and back-donation, forming coordinate covalent bonds with metal d-orbitals. The adsorption process, whether physisorption, chemisorption, or mixed-mode, creates a physical/chemical barrier limiting corrosive species access and modifying electrochemical reactions.

Recent advances in characterization and computational methods have substantially enhanced mechanistic understanding. XPS analysis of T. ruticarpum extract-treated steel confirmed FeO and FeN bond formation, providing direct evidence of chemisorption. DFT calculations of HOMO/LUMO energies, energy gaps, and electrostatic potential identify active adsorption sites and predict inhibition efficiency. MD simulations reveal adsorption configurations and binding energies, informing rational inhibitor design. The correlation between molecular descriptors and experimental performance establishes structure-activity relationships essential for inhibitor discovery and optimization. However, significant gaps persist in understanding green inhibitor behavior under realistic service conditions. Performance variability due to extract composition, seasonal variation, and extraction methods complicates standardization and quality control. Temperature, flow, and electrolyte composition effects on adsorption stability require systematic investigation across relevant industrial conditions. The dynamic nature of adsorption-desorption equilibria under fluctuating operational parameters demands consideration in inhibitor selection and deployment strategies.

Performance and Limitations of Green Inhibitor Systems:

The comparative analysis demonstrates that green corrosion inhibitors can achieve performance comparable to or exceeding traditional inhibitors under optimized conditions. Plant extracts exhibiting 85-95% efficiency in controlled laboratory media represent significant progress toward sustainable corrosion management. Hybrid systems achieving 92-98% efficiency through synergistic mechanisms approach or exceed traditional inhibitor performance, addressing earlier criticisms regarding green inhibitor limitations.

However, substantial challenges persist in translating laboratory performance to industrial application. Temperature sensitivity, particularly for physiosorbed inhibitors, limits applicability in elevated-temperature operations characteristic of oilfields and geothermal systems. Flow-induced desorption and erosion-corrosion interactions reduce inhibitor effectiveness in high-velocity pipelines. Performance variability due to extract composition and quality control issues complicates industrial acceptance. Scalability challenges including cost-effective extraction, formulation stability, and quality assurance require resolution for commercial deployment. The gap between laboratory and field performance reflects the complexity of real-world corrosive environments multicomponent electrolytes, fluctuating temperatures, hydrodynamic effects, and microbial activity that are difficult to replicate in controlled studies. Standardized testing protocols and field-relevant performance metrics are needed to enable meaningful comparison and selection of green inhibitors for specific applications. Life-cycle assessment and environmental fate studies, currently limited for most green inhibitors, are essential for comprehensive sustainability evaluation.

Digital Transformation and Data-Driven Discovery

The integration of computational modeling, machine learning, and data science approaches offers transformative potential for green inhibitor discovery and optimization. DFT calculations and MD simulations enable molecular-level understanding of inhibitor-metal interactions, guiding rational design of molecular structures with optimized adsorption properties. Machine learning models, trained on experimental data, can predict inhibitor performance, accelerate screening of candidate compounds, and identify structure-activity relationships governing efficacy.

Recent applications of artificial intelligence to corrosion inhibitor design have demonstrated prediction accuracy of $R^2 > 0.85$ for corrosion rate forecasting and inhibitor efficiency prediction. These approaches reduce experimental effort, enable exploration of vast chemical space, and provide mechanistic insights through feature importance analysis. Integration of data-driven discovery with experimental validation creates an iterative optimization cycle accelerating green inhibitor development. However, the effectiveness of computational approaches depends on availability of high-quality, standardized experimental data. Current limitations in data curation, reporting standards, and experimental reproducibility constrain model development and validation. Collaborative efforts to establish open-access databases, standardized testing protocols, and benchmarking frameworks are essential to realize the full potential of AI-driven corrosion inhibitor discovery. The development of field-relevant models incorporating environmental parameters, hydrodynamic effects, and long-term stability considerations represents the next frontier in digital transformation of corrosion management.

Future Directions and Recommendations:

Future research and development should prioritize several interconnected areas to advance green corrosion inhibitor technology from laboratory demonstration to industrial deployment.

First, standardized testing protocols and performance metrics must be developed to enable meaningful comparison across studies and materials, incorporating field-relevant conditions including temperature cycling, flow effects, and multicomponent electrolytes.

Second, mechanistic understanding of adsorption-desorption equilibria, protective film dynamics, and long-term stability requires systematic investigation under relevant service conditions.

Third, hybrid inhibitor systems should be optimized for specific industrial applications, balancing performance, cost, and environmental footprint. Scaling of nanoparticle and nanocomposite synthesis, formulation stability optimization, and quality assurance development are priorities for commercial deployment.

Fourth, integration of data-driven discovery with mechanistic understanding combining DFT, MD simulations, machine learning, and experimental validation offers accelerated inhibitor discovery and optimization.

Fifth, life-cycle assessment and environmental fate studies are needed to establish sustainability credentials of green inhibitors across their full lifecycle sourcing, manufacturing, use, and disposal. Regulatory frameworks and industry standards must evolve to incorporate green inhibitor performance metrics and environmental criteria.

Sixth, interdisciplinary collaboration across materials science, electrochemistry, green chemistry, computational modeling, and industrial engineering is essential to address the complex, multifaceted challenges of green corrosion inhibitor development and deployment.

Conclusion

This comprehensive review has systematically examined green corrosion inhibitors as sustainable approaches for metal protection in harsh environments. Corrosion imposes annual global costs of approximately $2.5 trillion, equivalent to 3-4% of GDP in industrialized nations, driving urgent need for effective, environmentally compatible mitigation strategies. Traditional inhibitors, while effective, pose significant environmental and health concerns, creating demand for sustainable alternatives derived from renewable, biodegradable sources. Plant-derived green inhibitors, encompassing extracts from Neem, Henna, Green Tea, and agricultural wastes, have demonstrated inhibition efficiencies exceeding 90% through adsorption-driven protective film formation. The rich phytochemical composition alkaloids, flavonoids, tannins, polyphenols provide heteroatoms (N, O, S) and conjugated π-systems essential for metal surface coordination. Adsorption mechanisms, whether physisorption, chemisorption, or mixed-mode, govern performance through formation of physical/chemical barriers limiting corrosive species access.

Hybrid inhibitor systems, combining green organics with inorganic additives or nanomaterials, represent a significant advancement, achieving 92-98% efficiency through synergistic mechanisms. The Org/Fe system demonstrated 92.53% efficiency compared to 82.55% for base extract, while silver nanoparticle hybrids achieved 97.9% efficiency. These systems offer enhanced adsorption strength, denser protective films, and multifunctional capabilities including anti-biofouling and selfhealing, addressing performance limitations of individual green inhibitors.

Advanced characterization techniques including EIS, potentiodynamic polarization, and XPS provide mechanistic understanding of inhibitor-metal interactions. Computational approaches including DFT and MD simulations enable molecular-level insight and rational design. Data-driven discovery through machine learning accelerates inhibitor screening and optimization, with prediction accuracy exceeding $R^2 > 0.85$.

Despite substantial progress, challenges persist in performance variability, temperature sensitivity, scalability, and standardization. Translation from laboratory to industrial application requires field-relevant testing protocols, quality assurance, and life-cycle assessment. Future research should prioritize standardized testing, mechanistic understanding under realistic conditions, hybrid system optimization, data-driven discovery, and interdisciplinary collaboration. With continued advancement and implementation, green corrosion inhibitors offer viable, sustainable pathways for corrosion management across oil and gas, marine, infrastructure, and emerging applications, delivering economic, environmental, and safety benefits consistent with global sustainability goals.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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