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EVALUATION OF *CITRUS SINENSIS* (ORANGE) PEEL EXTRACT AS A GREEN INHIBITOR FOR CARBON STEEL CORROSION IN HCl and H_2SO_4 SOLUTIONS

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ABSTRACT
This study investigated the corrosion inhibitory potential of *Citrus sinensis* (orange peel) extract on carbon steel in 1M hydrochloric and 1M sulphuric acid environments. Experimental results revealed that the extract exhibited notable inhibition efficiencies, reaching 76.92% in HCl and 72.97% in H_2SO_4 at 1.5 g/L concentration and 60°C. A clear inverse relationship between inhibitor concentration and corrosion rate was observed, highlighting the extract's concentration-dependent behaviour. The higher performance in chloride-rich media suggests enhanced adsorption due to favourable molecular interactions. These findings underscore the thermal stability and versatility of *Citrus sinensis* extract across varied acidic conditions, reinforcing its suitability for sustainable corrosion management. As a green inhibitor derived from agro-waste, it offers eco-friendly advantages, cost efficiency, and the potential for industrial integration. Overall, the extract presented a compelling case for scalable application in corrosion control systems where environmental safety and chemical robustness are priorities.

Keywords: Corrosion inhibition, Carbon-steel, Citrus sinensis, Inhibition efficiency, Corrosion rate

INTRODUCTION
Corrosion is an electrochemical process that gradually destroys metallic materials through chemical reactions with their environment. Among the various metals used in industry, carbon steel is especially vulnerable to corrosion especially when exposed to acidic conditions, such as those found in pickling, acid cleaning, oil well acidizing, and descaling operations. These environments often involve the use of hydrochloric acid (HCl) and sulphuric acid (H_2SO_4), which aggressively attack the steel surface, compromising structural integrity, operational safety, and economic efficiency (Popoola, 2019).

Historically, corrosion protection has relied heavily on synthetic inhibitors, many of which are effective but pose significant environmental and health risks mainly due to their toxicity, persistence, and non-biodegradability (Shehata et al., 2018). This has led to an increased global demand for green and sustainable alternatives that are not only effective but also environmentally benign (Morais et al., 2023).

Plant-derived substances have garnered widespread attention for utilization as potential corrosion inhibitors mainly because to their rich phytochemical composition and renewable nature. Fruit peels often discarded as agricultural waste are particularly promising because they contain a variety of organic compounds namely flavonoids, alkaloids, tannins, essential oils, and pectin. These compounds have demonstrated surface-active and antioxidant properties, making them suitable candidates for metal surface protection (Stango & Vijayalakshmi, 2018; Bandeira et al., 2025).

Citrus sinensis, also commonly known as sweet orange, is cultivated extensively across tropical and subtropical regions, including Nigeria. Its peel is an abundant agro-waste rich in bioactive molecules like limonene, hesperidin, and ascorbic acid. These compounds possess functional groups that can adsorb onto metal surfaces, potentially creating a protective barrier against acidic corrosion (Xavier & Vijayalakshmi, 2018; Ituen et al., 2021).

This study evaluated the corrosion inhibition performance of *Citrus sinensis* peel extract on carbon steel exposed to hydrochloric and sulphuric acid environments. By employing weight loss techniques, the study quantified its effectiveness and assessed its viability as a green corrosion inhibitor in industries.

LITERATURE REVIEW

The growing focus on sustainability in industrial practices has led to increased research in green corrosion inhibitors derived from plant extracts. These natural compounds offer a biodegradable, non-toxic alternative to synthetic inhibitors, aligning with the principles of green chemistry and environmental stewardship. Since 2018, a surge of research has focused on various plant species whose phytochemicals exhibit strong adsorption and protective capabilities on metal surfaces.

Recent studies have demonstrated that Azadirachta indica (neem) extract is highly effective in acidic environments. According to Popoola (2019), neem contains alkaloids and flavonoids that facilitate chemisorption onto mild steel surfaces, forming a protective barrier that significantly reduces corrosion rates. Similarly, Rosmarinus officinalis (rosemary) has shown promise due to its antioxidant-rich profile. A study by Bairwa (2024) reported inhibition efficiencies exceeding 85% in hydrochloric acid, attributing the performance to phenolic compounds and terpenes that interact with the metal surface.

Another notable example is Allium sativum (garlic), which is rich in sulphur-containing compounds. These molecules exhibit strong electron-donating properties, enhancing their ability to adsorb onto steel surfaces and suppress electrochemical reactions. Abdallah et al. (2018) found that garlic extract provided substantial protection in 0.5 M H_2SO_4, with inhibition efficiencies above 90%.

Laurus nobilis (bay leaf) and Terminalia arjuna have also been investigated for their corrosion-inhibiting properties. Bhattarai (2018) conducted immersion and electrochemical tests in both HCl and H_2SO_4 media, revealing that these extracts obey Langmuir and Temkin adsorption

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isotherms and act as mixed-type inhibitors. Their effectiveness was linked to the presence of tannins, saponins, and polyphenols that form monolayers on the metal surface.

In addition to plant leaves, biopolymers such as guar gum and cellulose derivatives have been explored. These high-molecular-weight compounds form viscous films that impede ion diffusion and stabilize the metal surface. Studies by Marzorati et al. (2019) emphasized the role of polysaccharides in enhancing corrosion resistance, especially in saline and acidic conditions.
Comparative analyses show that these inhibitors generally perform better in hydrochloric acid due to favourable chloride ion interactions that promote adsorption. However, some inhibitors like neem and garlic retain efficacy in sulphuric acid, suggesting versatility across corrosive environments.

In summary, recent literature highlights a diverse array of plant-based inhibitors ranging from herbs and spices to tree bark and biopolymers that offer high inhibition efficiency, environmental safety, and economic feasibility. Their mechanisms typically involve adsorption through functional groups such as $–NH_2$, –COOH, –OH, and aromatic rings, forming protective films that reduce metal dissolution.

METHODOLOGY

Metal coupon preparation

The methodology employed in this study involved the preparation of carbon steel coupons, extraction of the plant-based inhibitor, formulation of acid test solutions, corrosion testing, and data analysis. Carbon steel sheets were cut into rectangular coupons measuring 4 cm by 2 cm. A small hole was drilled into one corner of each coupon to allow for suspension during corrosion testing. These metal specimens underwent surface preparation by mechanical polishing with graded emery papers to remove rust and achieve a uniformly smooth surface. They were then washed thoroughly with ethanol, rinsed properly with distilled water, dried, and stored in airtight containers until further use.

Inhibitor collection and extraction

Fresh orange peels (Citrus sinensis) were collected from Eke-Oko Market in Anambra State, Nigeria. To ensure purity, the peels were rinsed with distilled water. The outer layer and seeds were removed, and the cleaned peels were dried in a mechanical oven at a temperature of 50°C to prevent thermal decomposition of bioactive compounds. Once dried, the samples were then pulverized using a mechanical grinder and sieved through a 150 µm mesh to ensure uniform particle size. A 500-gram portion of the powdered peel was immersed in 95% ethanol in a volumetric flask. This mixture was covered with aluminium foil to reduce solvent evaporation and allowed to stand for six hours to facilitate extraction. The extract was then filtered and concentrated using a water bath heated to 50°C, resulting in a gelatinous residue stored in airtight containers for further use.

Test solution preparation

To prepare the acidic test media, hydrochloric acid and sulphuric acid were diluted using distilled water to 0.5 M solutions for corrosion testing.

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Inhibition study

The inhibition study was performed at three distinct temperatures: room temperature (25°C), 45°C, and 60°C. For each condition, test solutions were prepared with inhibitor concentrations of 0.5 g/L, 1.0 g/L, and 1.5 g/L. The carbon steel coupons were suspended using Polytetrafluoroethylene (PTFE) strings to avoid contamination. Immersion lasted for 16 hours, with weight measurements recorded every four hours to monitor mass loss due to corrosion. Experiments at elevated temperatures were conducted using a temperature-controlled water bath.

Corrosion testing involved precise mass measurements taken before and after immersion, while the following formulas were used in calculating the corrosion rate (CR) and inhibition efficiency (% IE).

$$CR = \frac{534 * M}{\rho * A * t}$$

Where: M = Mass loss due to corrosion (mg), ρ = Density of carbon steel (mg/cm^3), A = Exposed surface area (cm^2), t = Immersion time (h)

$$\%\ \text{Inhibition Efficiency} = \left(\frac{W_o - W_i}{W_o}\right) * 100\ \%$$

Where: W_0 = Weight loss in the absence of inhibitor (blank solution), W_i = Weight loss in the presence of inhibitor

RESULTS AND DISCUSSION

Results

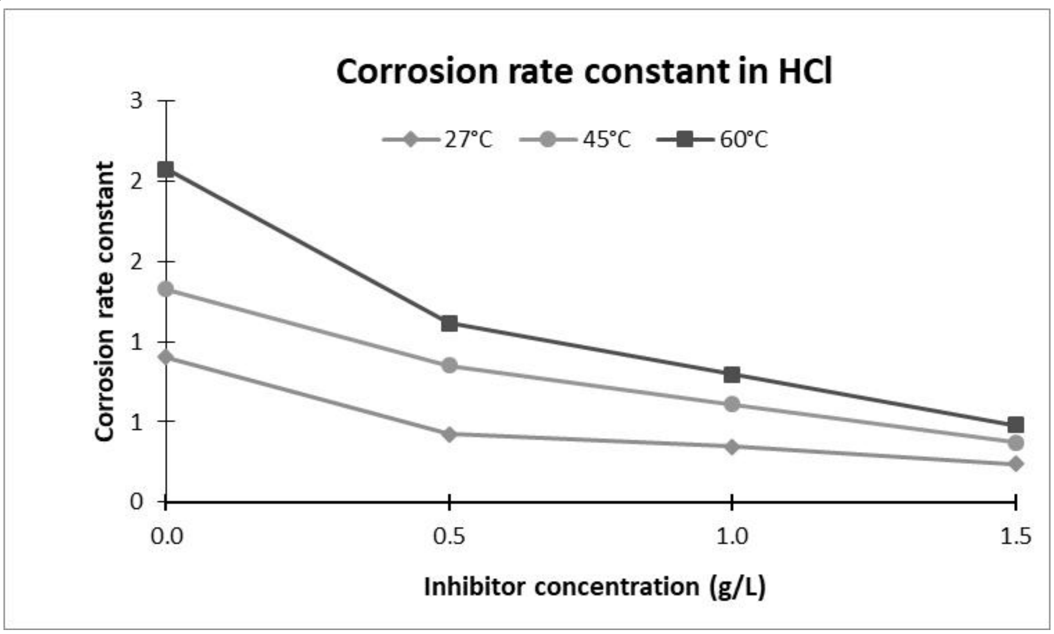

Fig. 1: Graph showing the corrosion rate constant in HCl

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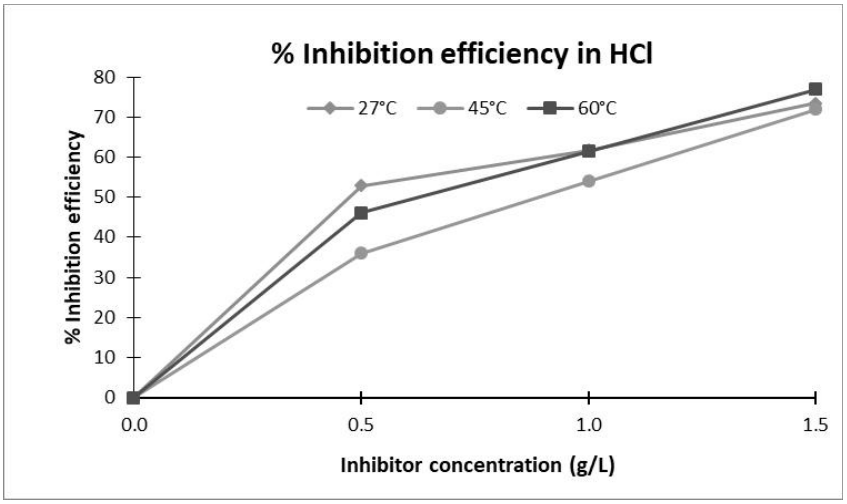

Fig. 2: Graph showing the % inhibition efficiency in HCl

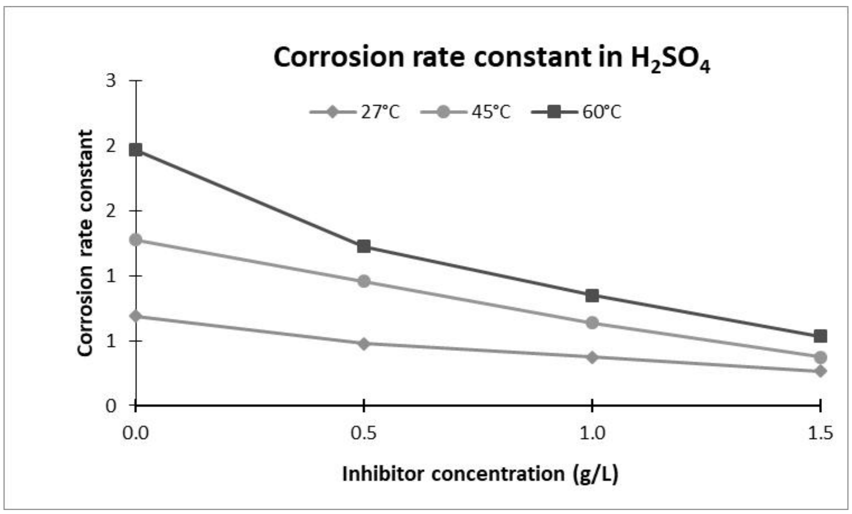

Fig. 3: Graph showing the corrosion rate constant in H_2SO_4

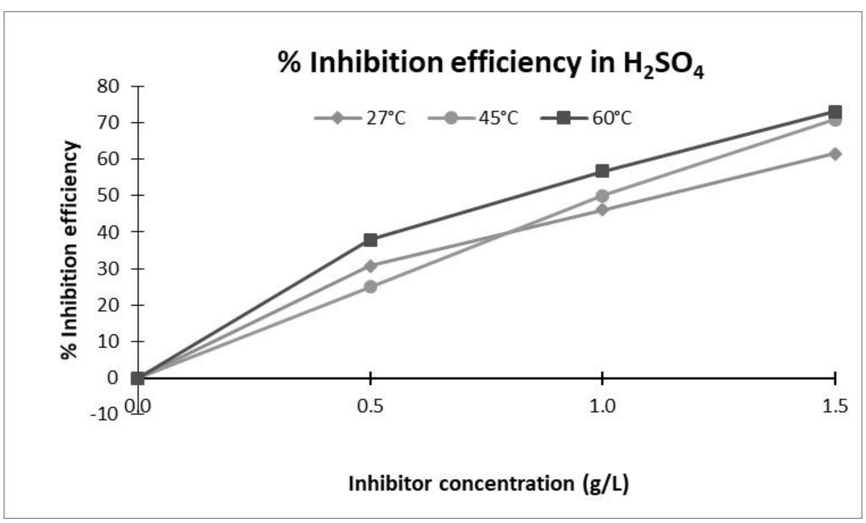

Fig. 4: Graph showing the % inhibition efficiency in H_2SO_4

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Discussion

Performance of inhibitor in hydrochloric acid (HCl)

The inhibition efficiency of *Citrus sinensis* extract in 1 M HCl shows a clear concentration-dependent behaviour across all temperatures tested. At 27°C, the efficiency increases steadily from 0.00% in the blank to 73.53% at the maximum concentration of 1.5 g/L. This trend is mirrored at elevated temperatures, with efficiency values rising to 72.00% at 45°C and peaking at 76.92% at 60°C. Interestingly, while one might expect inhibition to diminish at higher temperatures due to increased molecular activity and corrosion aggressiveness, the data indicate a sustained or even improved inhibitor performance with temperature. This implies thermal stability and enhanced adsorption strength of the extract's constituents, likely attributed to polar functional groups such as carboxyl and hydroxyl moieties found in flavonoids and phenolic compounds (Morais et al., 2023; Bandeira et al., 2025).

Corrosion rate constants in HCl further reinforce the inhibitor's efficacy. At 27°C, the uninhibited corrosion rate stands at 0.90 $mg/cm^2 \cdot h$, which drops significantly to 0.24 $mg/cm^2 \cdot h$ at 1.5 g/L inhibitor concentration. This trend persists as temperature increases: at 60°C, the rate decreases from 2.07 to 0.48 $mg/cm^2 \cdot h$. The inverse relationship between inhibitor concentration and corrosion rate reflects successful surface passivation by the organic molecules, likely forming a compact film that blocks active corrosion sites (Xavier & Vijayalakshmi, 2018; Ituen et al., 2021). Importantly, the extract maintains its protective capacity even as thermal agitation intensifies, highlighting its suitability for high-temperature industrial processes such as acid cleaning and metal treatment (Popoola, 2019).

In 1 M H_2SO_4, the inhibition efficiency of the *Citrus sinensis* extract also exhibits positive growth with increasing concentration and temperature, though generally lower than in HCl. At 27°C, the extract achieves 30.77%, 46.15%, and 61.54% inhibition efficiency for concentrations of 0.5, 1.0, and 1.5 g/L respectively. The efficiency improves further at higher temperatures, reaching 72.97% at 1.5 g/L and 60°C. These values affirm the extract's ability to resist the more oxidizing nature of sulphuric acid, even under elevated thermal conditions (Stango & Vijayalakshmi, 2018; Morais et al., 2023; Ali et al., 2021). The lower baseline efficiencies compared to HCl may stem from the larger ionic size and stronger acidity of sulphate ions, which could hinder molecular adsorption or disrupt protective film integrity (Shehata et al., 2018; Ezeamaku et al., 2019). Nonetheless, the upward trajectory with temperature suggests some level of thermal activation aiding molecular anchoring (Loto et al., 2020; Bandeira et al., 2025).

Corrosion rate measurements in H_2SO_4 reveal similar inhibitory trends. In the absence of inhibitor, corrosion rates climb from 0.69 $mg/cm^2 \cdot h$ at 27°C to 1.97 $mg/cm^2 \cdot h$ at 60°C. Upon inhibitor addition, the rates drop considerably: at 1.5 g/L, the rate decreases to 0.27 $mg/cm^2 \cdot h$ at 27°C and to 0.53 $mg/cm^2 \cdot h$ at 60°C. These reductions validate the extract's corrosion control capacity in sulphate-rich environments, indicating that its phytochemicals can successfully impede both electron transfer and hydrogen evolution reactions central to acid-induced metal degradation (Bandeira et al., 2025; Ituen et al., 2021; Ali et al., 2021). The efficient reduction of corrosion rate at elevated temperatures affirms the stability of the inhibition mechanism and highlights the extract's dual functionality—physicochemical adsorption and possible chemical reaction with the metal substrate (Morais et al., 2023; Loto et al., 2020).

Comparative Analysis Between HCl and H_2SO_4 Systems

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Across both acid media, *Citrus sinensis* extract shows consistent and concentration-dependent inhibition performance, with generally stronger effects in hydrochloric acid. The highest recorded efficiency in HCl is 76.92% at 1.5 g/L and 60°C, compared to 72.97% in H_2SO_4 under the same conditions. This disparity could be due to the extract's better molecular compatibility with chloride ions, which are smaller, more mobile, and possibly more conducive to surface film formation (Xavier & Vijayalakshmi, 2018; Popoola, 2019; Loto et al., 2020). In contrast, sulphate ions may compete with organic molecules for adsorption sites, slightly diminishing the extract's performance (Ezeamaku et al., 2019; Okoro & Nwankwo, 2024).

Corrosion rate constants also reflect this trend. In HCl, the rate drops by approximately 73% at 27°C and 77% at 60°C with full inhibitor dosage. In H_2SO_4, comparable reductions of ~61% and ~73% are observed respectively. These figures confirm that although the extract is marginally more effective in HCl, its performance in H_2SO_4 remains robust and industrially viable (Morais et al., 2023; Bandeira et al., 2025; Iheaturu & Chike, 2022).

Furthermore, the data suggest that temperature does not deteriorate the efficacy of the extract—in fact, it may enhance the adsorption and protective film stability. This thermal adaptability is crucial for scaling the application to environments where temperature fluctuations are frequent (Shehata et al., 2018; Loto et al., 2020).

The inhibition behaviour appears to follow Langmuir-type adsorption isotherm, suggesting monolayer coverage and uniform adsorption sites (Okoro & Nwankwo, 2024). The bioactive components such as limonene, tannins, flavonoids, and vitamin C possess multiple functional groups that facilitate strong interaction with the metal surface via hydrogen bonding, electron donation, and π-electron interactions (Ituen et al., 2021; Bandeira et al., 2025; Ezeamaku et al., 2019). These molecules likely act via a mixed inhibition mechanism, obstructing both anodic and cathodic processes (Popoola, 2019; Iheaturu & Chike, 2022).

Taken together, the data present *Citrus sinensis* peel extract as an effective green inhibitor with broad-spectrum corrosion control capabilities. Its reliable performance in both HCl and H_2SO_4, coupled with high thermal tolerance, makes it an eco-friendly and economically attractive alternative for metal protection in sectors such as chemical processing, water treatment, and infrastructure maintenance (Morais et al., 2023; Xavier & Vijayalakshmi, 2018; Okoro & Nwankwo, 2024).

CONCLUSION AND RECOMMENDATIONS

The current findings reaffirm the effectiveness of *Citrus sinensis* (orange peel) extract as a potent green corrosion inhibitor for carbon steel exposed to acidic conditions. Quantitative results across varied temperatures and concentrations underscore a clear inverse correlation between corrosion rate and inhibitor dosage, alongside a consistent increase in inhibition efficiency. Notably, the extract achieved up to 76.92% inhibition in hydrochloric acid and 72.97% in sulphuric acid at 1.5 g/L concentration and 60°C. This confirms not only the concentration-dependent mechanism of the inhibitor but also its thermal stability and resilience under elevated temperature conditions, which is a key advantage for industrial applications (Morais et al., 2023; Bandeira et al., 2025; Shehata et al., 2018; Ali et al., 2021).

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The corrosion rate constants dropped markedly with the introduction of the inhibitor, indicating robust surface passivation. Higher efficiencies in HCl suggest that the extract's bioactive compounds interact more favourably in chloride-rich media, likely due to smaller ionic size and higher mobility facilitating better adsorption onto the metal surface (Ituen et al., 2021; Okunzuwa, 2024). However, substantial inhibition in H_2SO_4 reinforces the extract's versatility across corrosive environments (Stango & Vijayalakshmi, 2018; Ezeamaku et al., 2019). The extract's mixed-type inhibition behaviour, encompassing both anodic and cathodic suppression, adds further credibility to its wide-ranging utility in chemical processing and infrastructure maintenance sectors (Ali et al., 2021; Morais et al., 2023; Ituen et al., 2021).

Environmentally, the use of orange peel as an agro-waste resource contributes to sustainable corrosion management, supports circular economy practices, and provides an accessible low-cost alternative to synthetic inhibitors. Its consistent performance across acid types and temperatures validates its potential for scalable deployment.

Recommendations

1. Mechanistic Studies: Further investigation into the adsorption behavior using spectroscopic and surface analysis techniques (e.g., SEM, EDX, FTIR, EIS) is recommended to confirm the nature and stability of the inhibitor film.
2. Long-Term Immersion Testing: Evaluate the durability and time-dependent performance of the extract under extended exposure to simulate real-life operating conditions.
3. Phytochemical Isolation and Optimization: Identify and isolate specific active compounds within orange peel that contribute most to inhibition, allowing for formulation of enhanced blends.
4. Application Feasibility: Assess compatibility with industrial systems, including flow dynamics, scaling behaviour, and reactivity with other chemicals commonly used in acid treatment processes.
5. Eco-certification and Standardization: Initiate steps toward environmental certification and standardizing extraction and dosage protocols for commercial use.
6. Synergistic Enhancement: Explore the potential of combining *Citrus sinensis* extract with other natural inhibitors or nanoparticles to amplify performance across broader chemical and temperature regimes.

In conclusion, *Citrus sinensis* extract has demonstrated reliable, adaptable, and sustainable corrosion inhibition. Its green chemistry profile, coupled with high inhibition efficiency and favourable kinetic responses, positions it as a valuable candidate for future adoption in environmentally responsible corrosion protection systems.

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