

Mild Steel Corrosion Inhibition by Aqueous and Ethanolic *Gmelina arborea* Leaf Extracts Prepared via Ultrasound-Assisted Extraction

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Abstract

Corrosion of mild steel in acidic environments is a significant industrial and environmental challenge, underscoring the need for effective, environmentally sustainable corrosion inhibitors. This study evaluates the corrosion-inhibitory performance of aqueous and ethanolic leaf extracts of Gmelina arborea on mild steel in 1.0 M HCl. Phytochemical screening revealed alkaloids, flavonoids, tannins, and phenols in both extracts, whereas saponins were present only in the aqueous extract. Corrosion inhibition was assessed using weight loss and potentiodynamic polarization techniques. Results showed that inhibition efficiency increased with extract concentration (0.25, 0.50, and 1.0 g·L⁻¹), with the ethanolic extract demonstrating superior performance, achieving a maximum inhibition efficiency of 95.93% (weight loss) and 51.73% (potentiodynamic polarization) at 1.0 g·L⁻¹. Potentiodynamic polarization indicated that both extracts function as mixed-type inhibitors. Langmuir adsorption isotherm modeling confirmed monolayer adsorption on the metal surface, with Gibbs free energy values of -23.44 to -27.44 kJ·mol⁻¹ indicating a mixed physisorption–chemisorption mechanism. These findings suggest that G. arborea leaf extract, especially its ethanolic extract, is a promising green corrosion inhibitor for mild steel in acidic environments.

Keywords: *Gmelina arborea*, green corrosion inhibitors, HCl solution, mild steel ultrasound-assisted extraction

1. Introduction

Metal corrosion is a significant issue affecting industries globally, posing both economic and environmental challenges. The International Organization for

Standardization (2020) defines corrosion as the chemical interaction between a metallic material and its surroundings, leading to changes in the metal's properties that may impair its function. This deterioration is particularly relevant for mild steel, a widely used construction material known for its low cost and excellent mechanical properties (Choudhary *et al.*, 2016). Its low corrosion resistance poses a challenge, especially in acidic environments, which are widely used in industrial processes. Corrosion is fundamentally an electrochemical process involving electron transfer between the metal and a conductive solution through redox reactions (Brycki *et al.*, 2018). During this process, metal atoms at the anode undergo oxidation, releasing electrons and depleting the metal surface. These electrons are accepted at the cathode during the reduction process. The combined anodic and cathodic reactions drive the overall corrosion process, gradually deteriorating the metal's structure (Harsimran *et al.*, 2021). The consequences of corrosion extend beyond metal degradation, as addressing it has a significant impact on industries and the environment, contributing to pollution, system contamination, greenhouse gas emissions, resource depletion, and infrastructure degradation. Economically, it leads to increased maintenance and repair costs, production losses, compromised product integrity, and reduced material lifespan (Thakur *et al.*, 2024). To mitigate corrosion, a range of prevention methods has been developed, including the use of corrosion inhibitors. They are categorized as organic or inorganic inhibitors based on their composition (Ma *et al.*, 2022; Daoudi *et al.*, 2024). Inorganic inhibitors, mostly made up of chromates, nitrites, phosphates, and molybdates, are widely used due to their stability and durability in corrosion protection (Khan *et al.*, 2024). However, their use is limited by associated toxicity, disposal issues, and environmental harm (Ahmed *et al.*, 2024). As a result, organic inhibitors have emerged as more sustainable and eco-friendly alternatives because they are derived from natural and biodegradable sources that align with the principles of green chemistry and sustainable development (Zamindar *et al.*, 2024).

Plant extracts, which can be classified as organic inhibitors, have garnered increasing attention due to their abundance, renewability, and cost-effectiveness. Their richness in phytochemical content makes them valuable for various biological and industrial applications (Daoudi *et al.*, 2024). The corrosion inhibition potential of plant extracts is mainly due to the presence of phytochemicals such as tannins, phenols, alkaloids, saponins, terpenoids, and flavonoids. These compounds contain polar functional groups that enable them to adsorb onto metal surfaces, reducing corrosion. These polar groups contain heteroatoms such as oxygen, nitrogen, or sulfur, in addition to

aromatic rings bearing π -electrons. These electron-rich sites serve as adsorption centers that promote the interaction with the positively charged surface of the metal (or its ions) (Dahmani *et al.*, 2024; Daoudi *et al.*, 2024; Kaur & Saxena, 2024; Prifiharni *et al.*, 2024).

Numerous plant materials have already been investigated for their promising corrosion-inhibiting properties, including species that can be found in the Philippines such as *Citrofortunella macrocarpa* (calamansi) (Arguelles *et al.*, 2020), *Curcuma longa* (turmeric), *Capsicum annuum* (red pepper) (Singh *et al.*, 2024) and *Allium sativum* (garlic) (Barreto *et al.*, 2017). The plant of interest in this study is *G. arborea* (Figure 1), a fast-growing deciduous tree found in the Philippines that is widely utilized for its timber. According to the Food and Agriculture Organization (2020), it is the top introduced tree species in the country, with a reported forest growing stock of 110.12 million cubic meters. Studies have highlighted its medicinal properties, including antioxidant, anti-diabetic, anti-inflammatory, antiulcer, analgesic activities (Warrier *et al.*, 2021). Numerous studies have identified various phytochemicals present in *G. arborea*. Khalid *et al.* (2022) identified different phytochemicals present in its leaves including alkaloids, flavonoids, tannins, saponins, and terpenoids—compounds known for their corrosion inhibition potential. Prior investigations into the corrosion inhibition properties of *G. arborea* have demonstrated promising results. For instance, Nnanna *et al.* (2014) reported a 96.1% inhibition efficiency in 1.0 M HCl of its bark extract, while Abakedi *et al.* (2018) documented a 78.59% efficiency in H₂SO₄ solutions for its root extract. However, studies conducted for the potential of *G. arborea* as a corrosion inhibitor remain limited. Leaves are particularly abundant in trees like *G. arborea*, which are often treated as waste despite their potential in producing valuable extracts. Rich in bioactive compounds, it is abundant, highly available, sustainable, and biodegradable, making it a promising resource for developing corrosion inhibitors.



Figure 1. Image of *G. arborea* tree utilized for sample collection

The efficiency of phytochemical extraction depends on factors such as the extraction method and the type of solvent used. Different extraction techniques are available, including conventional methods such as maceration, digestion, infusion, percolation, and decoction to more advanced techniques like Soxhlet extraction, accelerated solvent extraction, microwave-assisted extraction, ultrasound-assisted extraction (UAE), and supercritical fluid extraction (Miralrio & Vázquez, 2020; Dahmani *et al.*, 2024). In this study, UAE was selected since it is considered a green extraction technique, requiring less solvent, lower energy input, and shorter extraction times compared to conventional methods (Bitwell *et al.*, 2023). Moreover, solvent selection is equally crucial in the extraction process, as the yield and composition of plant extracts are dependent on the nature of the solvent. Plant materials contain compounds with diverse chemical characteristics and polarities, which may or may not dissolve in a particular solvent (Sultana *et al.*, 2009). Since many phytochemicals with corrosion inhibition properties possess polar functional groups, the use of polar solvents is logical and effective. Two extraction solvents, water and ethanol, are among the most commonly used extraction solvent since they are suitable in extracting a broad range of bioactive compounds (Fierascu *et al.*, 2021).

To date, no comparative assessment of aqueous versus ethanolic *G. arborea* leaf extracts prepared through ultrasound-assisted extraction has been conducted, leaving it underexplored. This study addresses this gap by testing the hypothesis that solvent polarity influences the phytochemical composition, adsorption behavior, and corrosion-inhibition efficiency of *G. arborea* leaf extracts. Given the wide applicability of water and ethanol in extracting bioactive compounds, this study evaluates the corrosion inhibition potential of *G. arborea* leaf extracts prepared using these two solvents. Thus, the aqueous and ethanolic extracts are compared in terms of their phytochemical profile and inhibition efficiencies, as measured through qualitative phytochemical screening, weight loss analysis, potentiodynamic polarization, and adsorption modeling.

2. Methodology

2.1 Extraction of *Gmelina Arborea* Aqueous and Ethanolic Leaf Extracts

For the preparation and extraction of the plant material, the method outlined by Sadat *et al.* (2021) was used as a reference with modifications. Fresh leaves of *G. arborea* were sourced from matured *G. arborea* trees in Tagoloan, Misamis Oriental in January 2025. Approximately two kg of fresh, green, mature leaves were chosen and harvested using random sampling technique. The harvested leaves were shade dried for one week and cleaned by washing with tap water, followed by rinsing with distilled water to remove dirt and impurities. The cleaned leaves were air-dried for seven days. After drying, the leaves were ground into fine powder and then sieved using a 1000 micron strainer to ensure uniform particle size. For the extraction process, the fine powder of the dried leaves was mixed with analytical-grade ethanol and distilled water at a plant material-to-solvent ratio of 1:10 (w/v). The mixture was placed in an ultrasonic bath (Digital Pro+ PS-10A) operating at 40 kHz for 30 minutes at $40\pm 5^\circ\text{C}$. After extraction, the sample was filtered to remove the solid residues. To remove excess solvents, the ethanolic extract underwent rotary evaporation (Stuart RE300) and further dried in the oven at 40°C . The final crude extracts were stored in air-tight containers, labelled accordingly, and stored in the refrigerator until further application in the succeeding analytical procedures.

2.2 Phytochemical Screening

Qualitative phytochemical screening was conducted to assess the extraction efficiency of the crude extracts. Both filtered aqueous and ethanolic extracts were screened for the presence of the following phytochemicals: alkaloids, flavonoids, tannins, phenols, terpenoids, and saponins. The screening followed the standard methods outlined by several studies (Yadav *et al.*, 2014; Maheshwaran *et al.*, 2024).

2.2.1 Alkaloids (Wagner's Test)

To test for the presence of alkaloids, 3-5 drops of Wagner's reagent (composed of 1.27 g of iodine and 2.00 g of potassium iodide in 100 mL distilled water) were added to 2 mL of the extracts. The formation of red or brown precipitate served as the test indicator (Maheshwaran *et al.*, 2024).

2.2.2 Flavonoids (Shinoda's Test)

A fragment of magnesium ribbon was added to 2 mL of the extracts followed by adding drops of concentrated hydrochloric acid. A solution of orange or red coloration served as the indicator for this test (Maheshwaran *et al.*, 2024).

2.2.3 Tannins and Phenols (Ferric Chloride Test)

Two milliliters (2 mL) of the extracts were treated with 2 mL of 5% ferric chloride solution. The development of a blue or green coloration served as the indicator of the presence of tannins and phenols (Maheshwaran *et al.*, 2024).

2.2.4 Terpenoids

Two milliliters (2 mL) of acetic anhydride and 2-3 drops of concentrated sulfuric acid were added to 2 mL of the extracts. The appearance of a deep red color served as the indicator for this test (Yadav *et al.*, 2014).

2.2.5 Saponins (Foam Test)

One milliliter (1 mL) of the extracts was added to 2 mL of distilled water and shaken vigorously. The persistence of a 1-cm foam layer after 10 minutes was used as a criterion for indicating saponins (Maheshwaran *et al.*, 2024).

2.3 Weight Loss Measurement

The method employed in this test is adapted from the approach of Shuaib-Babata *et al.* (2024) with modifications on the mild steel coupon dimensions. Mild steel coupons (Figure 2) with dimensions of 2.0 cm × 2.0 cm × 0.4 cm were prepared by abrading with sand paper of varying grits (120, 240, 400, 600, 1000), degreasing with ethanol, and rinsing with acetone. This measurement is performed in triplicates, so twelve (12) pre-cleaned metal coupons were weighed for its initial mass. The pre-weighed coupons were immersed in 50 mL of analytical-grade 1 M HCl solution as the control and 0.25, 0.50, and 1.0 g·L⁻¹ of ethanolic and aqueous *G. arborea* extracts as test solutions. These pre-weighed coupons were retrieved for weight analysis at 24-hour intervals in a span of three days. Each coupon was thoroughly rinsed with distilled water, gently scrubbed with a bristle brush, and rinsed with acetone. The final mass of each coupon was recorded.

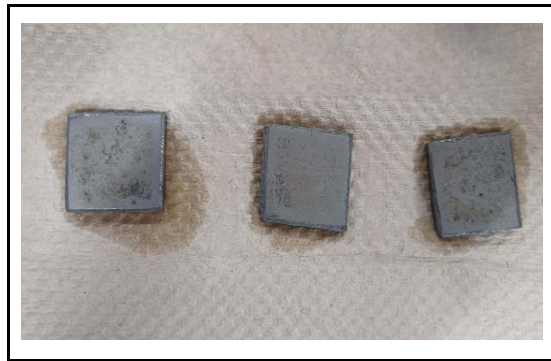


Figure 2. Mild steel specimens employed in corrosion testing

The weight loss (ΔW) in milligrams was calculated as the difference between the initial (W_i) and final weight (W_o) of the same coupons at each 24-hour interval (Equation 1).

$$\Delta W = W_i - W_o \quad (1)$$

This equation allows for the calculation of the corrosion rate (CR) and inhibition efficiency ($\%IE$) which is computed using Equations 2 and 3, respectively.

$$CR = \frac{\Delta W}{A \times t} \quad (2)$$

where t is the exposure time in hours, and A is the coupon area in cm^2 .

$$\%IE = \frac{CR_0 - CR_1}{CR_0} \times 100 \tag{3}$$

where CR_0 is the corrosion rate in the absence of the inhibitor, while CR_1 is the corrosion rate in the presence of an inhibitor.

2.4 Adsorption Isotherm Modeling

Adsorption isotherm modeling was conducted to evaluate the interaction between *G. arborea* inhibitor molecules and the mild steel surface in acidic media using the control and 0.25, 0.50, and 1.0 $\text{g} \cdot \text{L}^{-1}$ as test solutions. The extent of surface coverage (θ) was calculated from the inhibition efficiency ($\%IE$) obtained through weight loss measurements using Equation 4.

$$\theta = \frac{\%IE}{100} \tag{4}$$

To investigate the adsorption mechanism, three isotherm models were assessed: Langmuir, Temkin, and Freundlich. The linearized equations and corresponding parameters of these models are summarized in Table 1. For each isotherm, the correlation coefficient (R^2) was used to evaluate the goodness of fit. The model that yielded the highest R^2 value was considered the best-fitting isotherm, indicating the most accurate representation of the adsorption behavior between the inhibitor molecules and the mild steel surface under the experimental conditions. The correlation was done using the method of least squares.

Table 1. Linear equations used for Langmuir, Temkin, and Freundlich Adsorption Isotherm Modeling

Adsorption Isotherm Model	Linear Equation	References
Langmuir	$\frac{C}{\theta} = C + \frac{1}{K_{ads}}$	Abin-Bazaine <i>et al.</i> (2022) and Miralrio and Vázquez (2020)
Temkin	$\theta = K_{ads} \log \log \theta$	
Freundlich	$= \frac{1}{n} \log \log C + \log \log K_{ads}$	

In Table 1, C is the concentration of the inhibitor (in $\text{g}\cdot\text{L}^{-1}$), θ is the degree of surface coverage of the inhibitor, and K_{ads} is the adsorption equilibrium constant. To provide further insights into the spontaneity and nature of adsorption mechanism, standard free energy of adsorption (ΔG_{ads}^0) was calculated using Equation 5.

$$\Delta G_{ads} = -RT \ln(1000 K_{ads}) \quad (5)$$

where R represents the universal gas constant, T denotes absolute temperature, and 1000 is the concentration of water molecules in $\text{g}\cdot\text{L}^{-1}$.

2.5 Potentiodynamic Polarization

This corrosion measurement technique followed the method of Umoren *et al.* (2018) with minor modifications in the potentiometer used in the experiment. Another set of twelve mild steel coupons measuring $2.0 \text{ cm} \times 2.0 \text{ cm} \times 0.4 \text{ cm}$, with working surface area of 4.0 cm^2 , were utilized for the electrochemical measurement. The coupons were polished using sand paper of varying grits, degreased with ethanol, and rinsed with acetone prior to the experimentation. The experimental setup (Figure 3) was a three-electrode cell system, consisting of the mild steel coupon as the working electrode (WE), a graphite rod as the counter electrode (CE), and an Ag/AgCl reference electrode (RE). The electrochemical measurements were carried out using Rodeostat Model-8V potentiostat. The Rodeostat Web App software version 1.2.1 was employed to set the test parameters and obtain the polarization results.

To start the process, the mild steel working electrode, together with the reference and counter electrode, were immersed in the test solution for 15 minutes until stable open circuit potential (OCP) was attained. Once the OCP was reached, potentiodynamic polarization was carried out by scanning the potential from -250 mV to $+250 \text{ mV}$ relative to OCP, at a scan rate of 0.5 mV/s . This procedure was repeated for the test and control solutions.

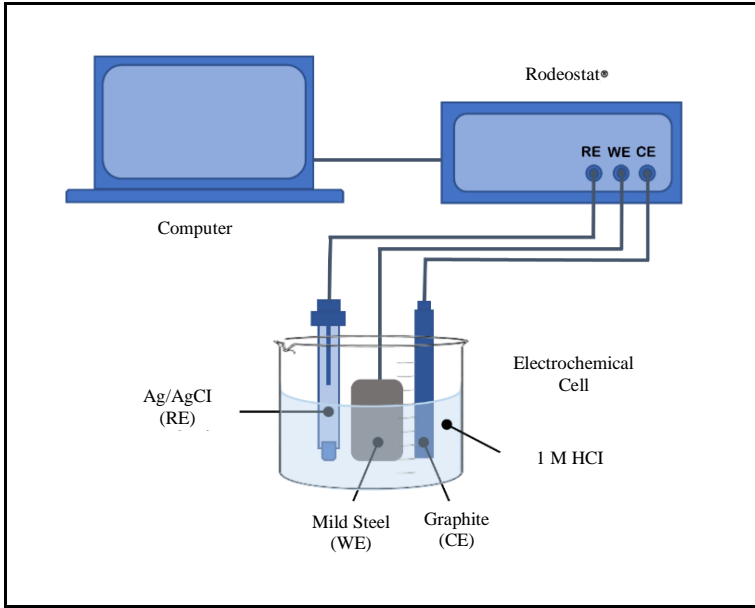


Figure 3. Experimental set-up for potentiodynamic polarization measurements

The linear segments of the anodic and cathodic polarization curves were extrapolated using the Tafel method to determine the corrosion current density (I_{corr}). The inhibition efficiency ($\%IE$) was then calculated using Equation 6.

$$\%IE = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (6)$$

where I_{corr} is the corrosion current density of the controlled solution while $I_{corr(inh)}$ is the corrosion current density of the solutions containing the inhibitor.

2.6. Statistical Analysis

Statistical analyses were performed using OriginPro 2025. A three-way Analysis of Variance (ANOVA) was conducted to evaluate the effects of solvent type (ethanol or water), extract concentration (0.25, 0.50, and 1.0 g·L⁻¹), and immersion time (24, 48, and 72 hours) on the inhibition efficiency obtained from the weight loss method. Each condition was tested in triplicate, and statistical significance was determined at $P \leq 0.05$. For conditions showing significant differences, Tukey's Honestly Significant Difference (HSD) post-hoc test was used to determine which group means differed. For adsorption

modelling, the method of least squares was used to determine the best-fitting plot with the most accurate description of the behavior between the metal-inhibitor interface.

3. Results and Discussion

3.1 Phytochemical Screening

Qualitative phytochemical profiling was conducted on both aqueous and ethanolic leaf extracts of *G. arborea*. As shown in Table 2, both extracts contained alkaloids, flavonoids, tannins, and phenols. However, saponins were only detected in the aqueous extract, while terpenoids were not observed in either extract. Figure 4 shows the photos of the different colors produced during the phytochemical screening of the samples.

Table 2. Phytochemical screening results of aqueous and ethanolic extract of *G. arborea* leaves

Phytochemical Constituents	Aqueous Extract	Ethanolic Extract
Alkaloids	+	+
Flavonoids	+	+
Tannins and Phenols	+	+
Terpenoids	–	–
Saponins	+	–

Key: '+' = Present; '-' = Absent

These findings align with previous work examining the phytochemical composition of *G. arborea* leaf extracts. Sreelakshmi (2023) reported a similar trend, noting that terpenoids were not detected in either extracts prepared through Soxhlet extraction. Likewise, Arya et al. (2025) noted the absence of saponins in the ethanolic leaf extract when compared with extracts obtained using other solvents, including water. The detection or absence of these phytochemicals is particularly relevant to corrosion inhibition, as many of these compounds contain functional groups capable of adsorbing onto metal surfaces and forming protective barriers (Mustapha et al., 2024).

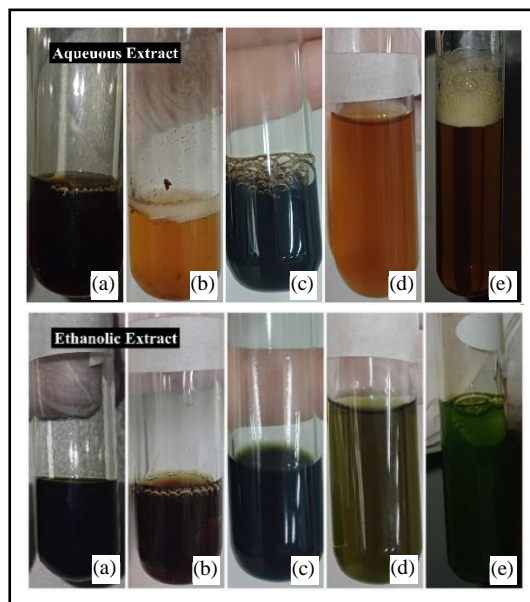


Figure 4. Phytochemical screening results of *G. arborea* leaves extract: alkaloids (a), flavonoids (b), tannins and phenols (c), terpenoids (d), and saponins (e)

3.2 Corrosion Inhibition Efficiency by Weight Loss Measurement

The corrosion rate and inhibition efficiency of mild steel in 1.0 M HCl solution, with and without the addition of *G. arborea* leaf extracts, were measured using the weight loss method. As shown in Table 3, both extracts reduced corrosion relative to the blank, with ethanollic extract exhibiting higher inhibition efficiencies across all concentrations and exposure times.

Table 3. Corrosion parameters obtained from weight loss method of mild steel in 1 M HCl at different concentrations and immersion times of aqueous and ethanollic *G. arborea* leaf extracts

Concentration (g·L ⁻¹)	24 hours		48 hours		72 hours	
	CR (mg cm ⁻² h ⁻¹)	%IE	CR (mg cm ⁻² h ⁻¹)	%IE	CR (mg cm ⁻² h ⁻¹)	%IE
Blank	1.9828	-	0.9439	-	0.6280	-
Aqueous <i>Gmelina arborea</i> leaf extracts						
0.25	0.3486	82.42	0.0827	91.24	0.0571	90.91
0.50	0.3413	82.79	0.0826	91.24	0.0550	91.25
1.0	0.2788	85.94	0.0503	94.67	0.0315	94.99
Ethanollic <i>Gmelina arborea</i> leaf extracts						
0.25	0.2646	86.66	0.0807	91.45	0.0532	91.52
0.50	0.2227	88.77	0.0592	93.73	0.0339	94.60
1.0	0.1804	90.90	0.0443	95.31	0.0256	95.93

The results show a consistent decrease in corrosion rate with the addition of *G. arborea* leaf extract up to the maximum tested concentration of $1.0 \text{ g}\cdot\text{L}^{-1}$. This trend in the corrosion rate is attributed to the increase in extract concentration, which implies that more extract molecules were adsorbed on the metal surface (Ofuyekpone *et al.*, 2023). To verify these observations, a three-way ANOVA followed by Tukey's HSD post-hoc test was performed, confirming that the reductions in the corrosion rate were statistically significant ($p < 0.05$). The following subsections further discuss the effects of concentration, immersion time, and solvent type on the corrosion inhibition performance.

3.2.1 Effect of Concentration

The influence of extract concentration on corrosion behavior was evaluated by comparing the corrosion rates of mild steel in uninhibited (blank) and inhibited solutions. As shown in Figure 5, both aqueous and ethanolic extracts of *G. arborea* lowered the corrosion rate relative to the blank solution. Notably, the corrosion rate decreased progressively with increasing inhibitor concentration. Statistical analysis using three-way ANOVA confirmed that concentration had a significant effect on inhibition efficiency, with each increase in extract concentration yields a statistically significant improvement in inhibition performance ($p < 0.001$). This can be attributed to the likelihood that at higher inhibitor concentrations, there is an increase in the molecules adsorbing onto the metal surface, forming a protective layer that reduces corrosion rates (Wang *et al.*, 2015).

This concentration-dependent trend observed in this study is consistent with previous findings of plant-based corrosion inhibitors. Xu *et al.* (2019) reported that although the corrosion inhibition of aqueous *Ligustrum vulgare* leaf extract improved with increasing concentration, the rate of improvement plateaued beyond $1.0 \text{ g}\cdot\text{L}^{-1}$, suggesting a saturation point beyond which no significant additional benefits occur. Similarly, Zhang *et al.* (2014) reported that aqueous pomegranate husk extract demonstrated peak inhibition performance near this concentration, reinforcing the idea that $1.0 \text{ g}\cdot\text{L}^{-1}$ represents a practical and effective upper limit for many plant-based inhibitors. These findings support the result of the current study, indicating that *G. arborea* leaf extract follows a similar trend, with maximum inhibition efficiency being observed at the highest tested concentration of $1.0 \text{ g}\cdot\text{L}^{-1}$.

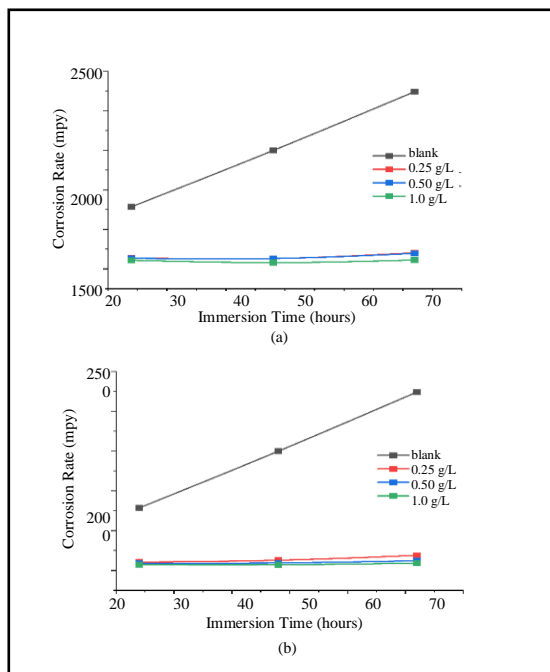


Figure 5. Effect of aqueous (a) and ethanolic (b) *G. arborea* extract concentration on corrosion rate of mild steel over time in 1 M HCl

The performance of *G. arborea* as a corrosion inhibitor is further supported by related literature on other plant-based inhibitors. Marsoul *et al.* (2020) demonstrated that *Punica granatum* bark extract substantially reduced the corrosion rate, decreasing from $0.5468 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ (blank) to $0.0712 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at $1 \text{ g}\cdot\text{L}^{-1}$ after 6 hours of immersion. Zubairu *et al.* (2020) observed comparable improvements when using *Polyalthia longifolia* leaf extract, with corrosion rates decreasing from $1.2\text{--}0.8 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ in the uninhibited solution to $0.7\text{--}0.3 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ upon addition of the inhibitor. Likewise, Zaher *et al.* (2020) reported that *Ammi visnaga* seed extract lowered the corrosion rate from $1.135 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ (blank) to $0.1929 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at $1 \text{ g}\cdot\text{L}^{-1}$ after 12 hours. These results collectively demonstrate that the corrosion rates and inhibition efficiencies achieved by *G. arborea* leaf extracts fall well within the range of other plant-based inhibitors, underscoring its potential as a sustainable corrosion-inhibiting material.

3.2.2 Effect of Immersion Time

The effect of immersion time on the inhibition efficiency of the extracts is illustrated in Figure 6. Across all immersion times, inhibition efficiency was found to increase with concentration. The maximum inhibition efficiencies recorded were 94.99% and 95.93% for the aqueous and ethanolic extracts, respectively, both at the optimal concentration of 1.0 g·L⁻¹ after 72 hours of immersion.

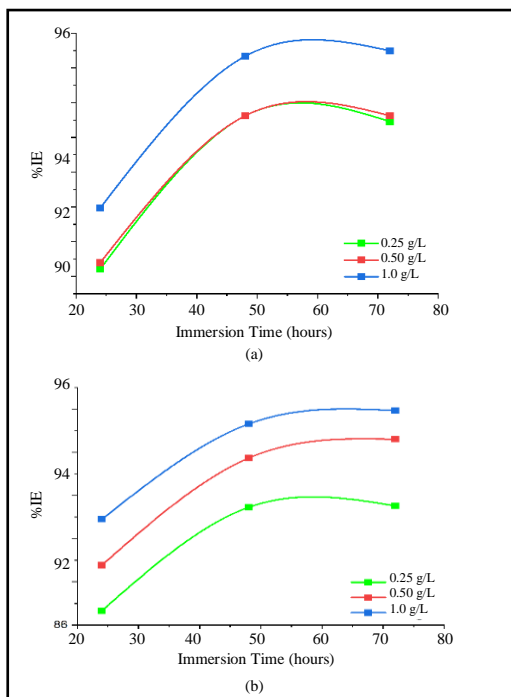


Figure 6. Inhibition efficiency of aqueous (a) and ethanolic (b) *G. arborea* leaf extracts on mild steel in 1 M HCl at varying concentrations and immersion times

Tukey's HSD post-hoc comparisons revealed that there are significant differences between 24 and 48 hours and between 24 and 72 hours ($p < 0.0001$ for both), whereas no significant difference was observed between 48 and 72 hours ($p = 0.6887$). This indicates that there is a plateau in inhibition performance beyond 48 hours. This plateau suggests that near-maximum surface coverage had been achieved during this period and further immersion time does not result in a significant increase in inhibition efficiency. This behavior reflects the formation of a stable and saturated protective film on the

metal surface, which prevents further adsorption of inhibitor molecules or additional corrosion activity (Kabyzbekova *et al.*, 2025).

Similar saturation behavior has been reported in other plant-based inhibitors, such as *Codiaeum variegatum* leaf extract, which exhibited maximum inhibition at 24 hours, with no further improvement at longer exposure times (Solanki *et al.*, 2025). Likewise, Deyab and Guibal (2020) observed that the efficiency of *Taraxacum officinale* extract increased with contact time up to 7 days and then slightly decreased beyond this time. In the present study, the plateau beyond 48 hours suggests that the inhibitor has reached its maximum protective capacity under the tested conditions, and further immersion time does not significantly enhance inhibition efficiency.

3.2.3 Solvent Effect

A significant difference in inhibition efficiency was observed between the ethanol and aqueous solvent systems used to extract *G. arborea* leaf compounds. Tukey's post hoc test indicated that the ethanolic extract exhibited significantly greater inhibition than the aqueous extract, with a mean difference of -2.61 ($p < 0.0001$). Both extracts were found to contain key phytochemicals associated with corrosion inhibition, namely, alkaloids, tannins, phenols, and flavonoids (Table 2). Their difference lies in the presence of saponins, which were only identified in the aqueous extract. Despite the absence of saponins, the ethanolic extract consistently showed better corrosion inhibition performance, as shown in Table 3. This observation aligns with findings from other studies. For example, Mandawara and Chaturvedi (2023) reported that the ethanolic extract of *Tinospora cordifolia* exhibited superior corrosion inhibition on copper compared to its aqueous counterpart. This superiority is attributed to the greater solubility of active compounds, such as alkaloids, flavonoids, and tannins, in ethanol, which enhances their adsorption on the metal surface. Similarly, Kumar *et al.* (2016) and Umoren *et al.* (2018) relate the improved inhibition performance of various vegetable and fruit by-products and date palm leaves and seeds ethanolic extracts to their ability for higher solubility of organic compounds compared to aqueous extracts. Aqueous extracts may suffer from dilution effects or lower solubility of key constituents, thus reducing their corrosion-inhibiting potential (Hart *et al.*, 2023). Moreover, the presence of saponins in aqueous extracts does not necessarily equate to better corrosion inhibition, as interactions at the metal interface significantly influence inhibition efficiency. Saponins may interfere with the adsorption of more potent inhibitors like flavonoids and tannins. Their foaming and amphiphilic nature may hinder

effective film formation on metal substrates (Oliveira *et al.*, 2018). Therefore, the superior performance of ethanolic extracts, despite the absence of saponins, can be attributed to the higher concentrations and stronger adsorption of other phytochemicals responsible for corrosion inhibition.

Overall, the inhibition performance of *G. arborea* leaf extracts is governed by the combined effects of concentration, immersion time, and solvent type. Higher concentrations provide more adsorbing molecules, enabling more complete surface coverage, which explains the strong concentration-dependent behavior observed in both extracts. Immersion time further enhances inhibition efficiency by allowing progressive film development, but the plateau beyond 48 hours indicates that the metal surface becomes saturated once optimal coverage is reached. Solvent type also influences performance, with the ethanolic extract achieving higher inhibition efficiencies at all concentrations and immersion times; this can be attributed to the possible higher concentrations and stronger adsorption of phytochemicals responsible for corrosion inhibition. These findings suggest that, although both extracts follow the same mechanistic trend, the ethanolic extract attains maximum protective coverage more efficiently.

3.3 Electrochemical Evaluation via Potentiodynamic Polarization

The electrochemical parameters, namely corrosion current (I_{corr}), corrosion potential (E_{corr}), and the corresponding inhibition efficiency (%IE) obtained from potentiodynamic polarization curves (Figure 7) are summarized in Table 4. The data clearly show that the addition of both aqueous and ethanolic *G. arborea* leaf extracts to the corrosive 1.0 M HCl medium reduces the corrosion rate of mild steel, as evident from the reduced I_{corr} values observed in the presence of both extracts compared to the uninhibited blank solution. The highest inhibition efficiencies recorded through polarization measurements were 38.00% for the aqueous extract and 51.73% for the ethanolic extract.

Table 4. Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M HCl solutions containing different concentrations of *G. arborea* leaf extracts

Extract	Concentration (g·mL ⁻¹)	E_{corr} (mV)	I_{corr} (A)	β_c (mV/dec)	β_a (mV/dec)	%IE
Blank	pure	-149.94	245.81	-356.51	421.05	-
	0.25	-96.52	159.07	-264.19	268.62	35.29
Aqueous	0.50	-97.37	157.94	-260.03	268.62	35.75
	1.0	-70.32	152.41	-263.19	224.23	38.00
	0.25	-93.85	144.31	-251.76	216.60	41.29
Ethanolic	0.50	-83.85	139.73	-242.48	216.12	43.15
	1.0	-72.34	118.66	-207.48	175.32	51.73

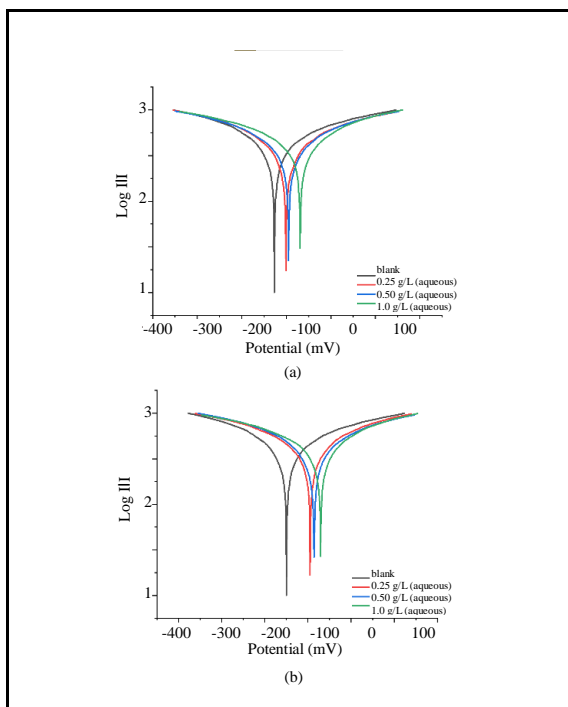


Figure 7. Potentiodynamic polarization plots for mild steel in 1 M HCl without and with aqueous (a) and ethanolic (b) *G. arborea* leaf extracts

A clear concentration-dependent trend is also observed in the polarization results. For both extracts, increasing the concentration from 0.25 to 1.0 g·L⁻¹ resulted in a progressive increase in inhibition efficiency. For the aqueous extract, %IE increased from 35.29% at 0.25 g·L⁻¹ to 38.00% at 1.0 g·L⁻¹, while ethanolic extract showed a stronger increase, from 41.29% to 51.73% over the same range. This behavior is attributed to enhanced surface coverage by the inhibitor molecules at higher concentrations, which leads to the increase in inhibition efficiency (Fathima & Sethumanickam, 2017).

These results follow the same increasing trend observed in the weight loss method, although the actual inhibition values were comparatively lower. This large difference between methods has been documented in several corrosion studies. For instance, Chen *et al.* (2013) reported higher inhibition efficiencies from weight loss data when using *Ginkgo biloba* extracts, attributing the discrepancy to the longer exposure duration in weight loss tests, which allows for more complete and stable protective film formation. Similarly, Patrascu *et al.* (2021) found that electrochemical techniques often underestimate

inhibition performance, as they capture instantaneous behavior rather than cumulative effects. These findings underscore the value of using both methods to comprehensively evaluate corrosion inhibition behavior.

To assess the type of inhibition mechanism, the change in corrosion potential was analyzed. It is generally accepted that if the shift in E_{corr} in the presence of an inhibitor is less than ± 85 mV compared to the blank, the inhibitor is considered to be of mixed-type (Ofuyekpone et al., 2023). As shown in Table 4, the maximum shifts in E_{corr} were -72.34 mV for the ethanolic extract and -70.32 mV for the aqueous extract. Since both values fall within the ± 85 mV threshold against the blank, it can be concluded that *G. arborea* leaf extracts act as mixed-type inhibitors, simultaneously influencing both anodic and cathodic reactions during the corrosion process

3.4 Adsorption Isotherm

To investigate the adsorption mechanism of aqueous and ethanolic *G. arborea* leaf extracts on mild steel, the experimental data were fitted to three commonly used adsorption isotherm models: Langmuir, Temkin, and Freundlich. The correlation coefficients (R^2) obtained from the linear plots provide insight into the suitability of each model. As shown in Table 5, the Langmuir isotherm model provides the best fit to the experimental data ($R^2 \approx 0.99$), indicating that the adsorption process primarily follows a monolayer adsorption mechanism on a homogeneous surface. This implies that once surface saturation is reached, adsorption becomes predictable, allowing for the estimation of the effective inhibitor dosage for corrosion control application.

Table 5. Correlation coefficients from Langmuir, Temkin and Freundlich isotherm for mild steel in 1 M HCl in the presence of *G. arborea* leaf extracts

Extract	Immersion Time (hours)	R^2		
		Langmuir	Temkin	Freundlich
Aqueous	24	0.99531	0.77434	0.77592
	48	0.99965	0.75201	0.75205
	72	0.99922	0.81217	0.81341
Ethanolic	24	0.99997	0.98709	0.98557
	48	0.99999	0.98920	0.98799
	72	1.0000	0.94997	0.94759

Although Langmuir provides best overall fit, the relatively high R^2 values obtained for Temkin and Freundlich model, particularly for the ethanolic extract, suggest that the adsorption process involves some degree of surface heterogeneity and adsorbate-adsorbate interactions. This behavior is expected

for plant-based inhibitors, where multiple phytochemical constituents are present. Figure 8 shows the Langmuir adsorption isotherm plots for the different concentrations of aqueous and ethanolic *G. arborea* leaf extracts at varying immersion times.

Table 6 reveals that ethanolic extract exhibits consistently higher adsorption equilibrium constants (K_{ads}) and slightly more negative Gibbs free energy of adsorption (ΔG^0_{ads}) values than the aqueous extract. These indicate that adsorption from ethanolic extract is both stronger and more spontaneous, which is consistent with the performance observed in the gravimetric and electrochemical tests.

Table 6. Langmuir adsorption isotherm and thermodynamic parameters for adsorption of aqueous and ethanolic *G. arborea* leaf extract on mild steel in 1 M HCl

Extract	Time (hours)	Slope	Intercept	K_{ads} ($L \cdot g^{-1}$)	ΔG^0_{ads} ($kJ \cdot mol^{-1}$)
Aqueous	24	1.00362	0.07230	13.83	-23.62
	48	1.03934	0.01983	50.43	-26.83
	72	1.03310	0.02261	44.23	-26.50
Ethanolic	24	1.08174	0.01870	53.48	-26.97
	48	1.03402	0.01551	64.47	-27.44
	72	1.02603	0.01620	61.73	-27.33

The variation of K_{ads} over time reflects the dynamic interaction between the inhibitor molecules and the mild steel surface. As shown in Table 6, an increase in K_{ads} was observed from 24 to 48 hours suggesting an enhancement in adsorption affinity as a more stable and organized inhibitor film develops. The Langmuir model describes adsorption as a dynamic equilibrium between adsorption and desorption rates, dependent on the number of available and occupied sites. Thus, the increase in K_{ads} suggests more efficient surface coverage as immersion time increases. In contrast, a decrease in K_{ads} from 48 to 72 hours may be attributed to surface site saturation, leading to reduced adsorption efficiency. This decline could result from steric hindrance or site blocking, where the binding strength per site diminishes as more inhibitor molecules occupy the surface (Shimizu & Matubayasi, 2023).

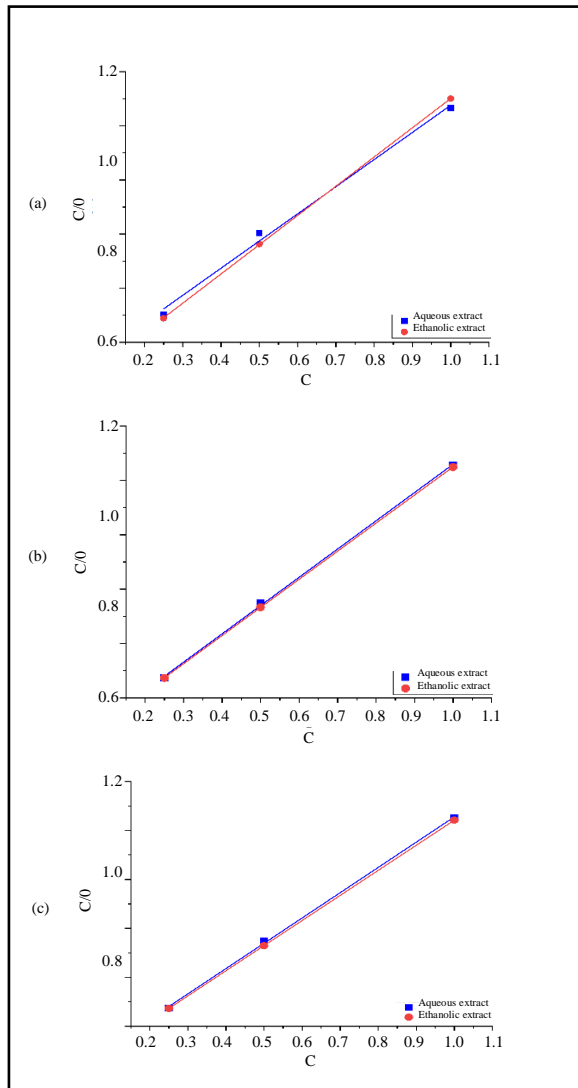


Figure 8. Langmuir adsorption isotherm plot with different concentrations of aqueous and ethanolic *G. arborea* leaf extracts at 24 hours (a) 48 hours (b) and 72 hours (c) immersion time

The ΔG^0_{ads} , presented in Table 6 were negative across all time points, confirming that the adsorption process is spontaneous (Phuyal *et al.*, 2024). Typically, ΔG^0_{ads} values of around -20 kJ/mol or less are associated with physisorption, involving weak van der Waals or electrostatic forces, while values around -40 kJ/mol or more negative indicate chemisorption, involving

stronger covalent or ionic bonding (Dibetsoe *et al.*, 2015). In this study, the obtained values range from -23.62 to -27.44 kJ/mol, indicating a mixed adsorption mechanism or the combination of physical and chemical interactions between the inhibitor molecules and the metal surface. This suggests that the inhibitor first adsorbs rapidly through physisorption, allowing quick occupation of active sites, followed by the development of stronger interactions characteristic of chemisorption. This dual behavior enhances film stability over prolonged immersion and is advantageous for real-world applications, where both fast film formation and long-term durability are desirable. Similar observations were reported by Li *et al.* (2022) for Perilla seed extract, where a ΔG^0_{ads} of -22.70 kJ/mol was found to indicate dual adsorption behavior.

4. Conclusion and Recommendation

The findings of this study demonstrate that both aqueous and ethanolic *G. arborea* leaf extracts are effective green corrosion inhibitors for mild steel in 1.0 M HCl. The extracts achieved high inhibition efficiencies, with weight loss measurements reaching up to 95.93% and potentiodynamic polarization measurements yielding up to 51.73% for the ethanolic extract. Phytochemical analysis confirmed the presence of alkaloids, flavonoids, tannins, and phenols, compounds known to adsorb onto metal surfaces and contribute to corrosion inhibition. While the ethanolic extract consistently exhibited higher inhibition efficiency, likely due to the greater solubility and availability of active constituents, the aqueous extract also demonstrated substantial performance, highlighting its value as a low-cost and environmentally benign alternative.

Both gravimetric and electrochemical evaluations showed that inhibition efficiency increased with inhibitor concentration and immersion time, and electrochemical results indicated that the extracts act as mixed-type inhibitors. Adsorption data followed the Langmuir isotherm, and the calculated ΔG^0_{ads} values confirmed a spontaneous mixed physical-chemical adsorption mechanism. Overall, the results support the potential of *G. arborea* leaf extracts, particularly the ethanolic extract, as sustainable corrosion inhibitors for acidic environments.

These findings also hold practical relevance, as mild steel is routinely exposed to acidic solutions in industrial operations such as acid cleaning, pickling,

descaling, and enhanced oil recovery. Given the abundance and biodegradability of *G. arborea*, its application as a corrosion inhibitor aligns with green chemistry principles and contributes to Sustainable Development Goals.

Further research on *G. arborea* leaf extracts should focus on quantifying active corrosion-inhibiting compounds using techniques such as GC-MS, FTIR, or HPLC. Additional studies are recommended to evaluate the extracts across various corrosive environments, temperatures, pH levels, exposure durations, and metal types to assess robustness. Broader extract concentrations are recommended to improve adsorption isotherm modeling. Long-term and field trials are needed to validate its practical effectiveness. The superior performance of ethanolic extract suggests potential for commercial applications, backed by environmental and economic assessments. Finally, advanced techniques such as SEM, EDS, and XPS are recommended to confirm adsorption mechanisms and film formation, thereby strengthening the scientific foundation for the sustainable industrial use of plant-based inhibitors.

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