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Research Article

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Posted Date: February 10th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-8491725/v1>

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Additional Declarations: No competing interests reported.

**Green corrosion inhibition of carbon steel in 10% (v/v) HCl solution using
cagaita (*Eugenia dysenterica*) extract**

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Abstract

Corrosion of carbon steel in acidic environments is a major industrial problem with significant economic and environmental impacts. In this study, an innovative and sustainable corrosion inhibition strategy is proposed using an aqueous extract of cagaita (*Eugenia dysenterica*), a native fruit from the Brazilian Cerrado—one of the largest and most biodiverse biomes worldwide.

Electrochemical measurements in 10 wt% HCl showed that the cagaita extract reduces the corrosion current density from 8.51×10^{-4} to $0.68 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ at $0.3 \text{ g}\cdot\text{L}^{-1}$, corresponding to an inhibition efficiency of 80–92%. Minor displacement of the corrosion potential ($\approx 7 \text{ mV}$), together with reductions in both anodic and cathodic Tafel slopes, indicates a mixed-type inhibition mechanism governed by adsorption. Adsorption behavior followed the Freundlich isotherm ($R^2 = 0.9973$), while the Langmuir model yielded a high affinity constant ($K_L = 21.99 \text{ L}\cdot\text{g}^{-1}$) and near-unity surface coverage. The estimated adsorption free energy ($\Delta G^\circ_{\text{ads}} \approx -31.6 \text{ kJ}\cdot\text{mol}^{-1}$) and the decrease in activation energy from 53.8 to 48.6 $\text{kJ}\cdot\text{mol}^{-1}$ confirm strong adsorption and surface-blocking effects.

Spectroscopic analyses confirmed the predominance of phenolic compounds, mainly epicatechin and quercetin, supporting the use of biodiversity-rich biomes such as the Brazilian Cerrado as valuable sources of green and effective corrosion inhibitors.

Keywords: *Eugenia dysenterica*; Green corrosion inhibitor; Carbon steel; Sustainable materials; Cagaita extract

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Introduction

Carbon steel is extensively used in industrial applications due to its favorable mechanical properties and low cost; however, it is highly susceptible to corrosion in acidic and chloride-containing environments, leading to severe economic losses estimated at approximately 3–4% of the global GDP [1]. In the oil, gas, and chemical industries alone, corrosion represents one of the most critical operational challenges, with associated costs estimated to reach approximately USD 170 billion per year [1–2]. On a global scale, the total annual cost of corrosion has been estimated at nearly USD 2.5 trillion, corresponding to approximately 3.4% of the global GDP [3]. The corrosion of carbon steel in acidic and chloride-rich environments accelerates material degradation, promoting metal dissolution, localized corrosion, and premature failure of structural components. As a result, corrosion compromises mechanical integrity, reduces service lifetime, and increases maintenance costs, safety risks, and environmental concerns associated with steel-based systems [2–5].

In this context, many industrial applications have increasingly relied on naturally derived corrosion inhibitors as a sustainable alternative to conventional chemical treatments. Plant extracts have been widely investigated due to their low cost, availability, and environmentally benign nature, as well as their richness in organic compounds containing heteroatoms and functional groups capable of interacting with steel surfaces. Recent studies highlight that such eco-friendly inhibitors can effectively mitigate corrosion in aggressive acidic environments while reducing environmental and health concerns associated with synthetic inhibitors [5,6].

According to frontier molecular orbital theory, the corrosion inhibition performance of organic molecules is closely related to their electronic structure. The highest occupied molecular orbital (HOMO) describes the electron-donating ability of the inhibitor, whereas the lowest unoccupied molecular orbital (LUMO) is associated with its electron-accepting capability. The energy gap between these orbitals ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) serves as an important reactivity descriptor, where smaller gap values indicate enhanced electronic activity and more favorable charge-transfer interactions with the metal surface. These concepts are schematically summarized in Figure 1 [7–9].

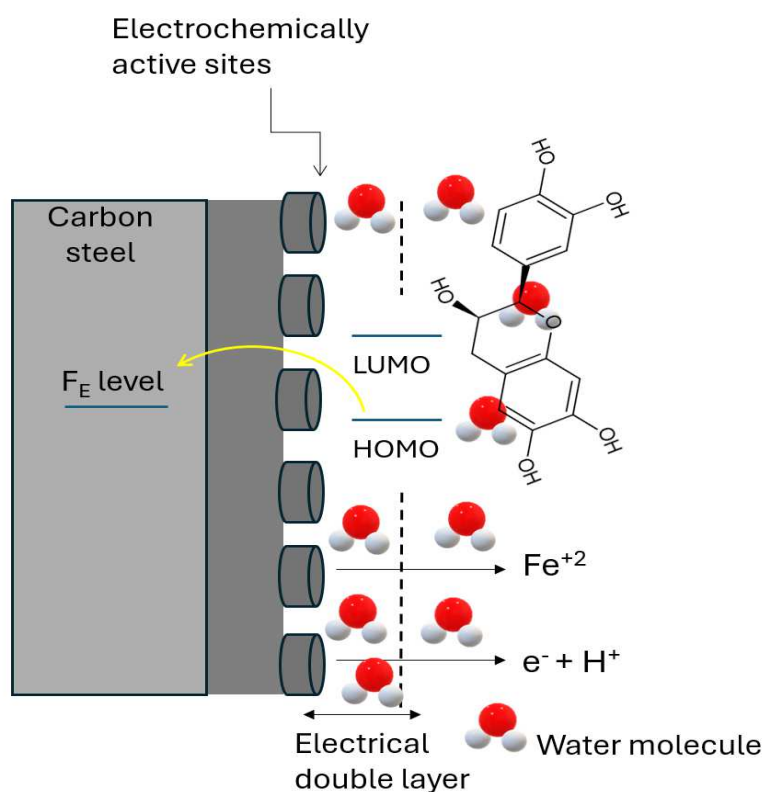


Figure 1- Schematic representation of the proposed corrosion inhibition mechanism of phenolic compounds present in the cagaita extract on carbon steel in acidic medium.

In addition, organic molecules containing π -electron systems, such as C=C and C $\equiv$ C bonds or aromatic rings, present delocalized electron density that favors charge-transfer interactions with the metal surface. In contrast, σ -bond electrons are more localized and generally contribute less to electronic interaction with the metal. Therefore, the presence of π -electrons plays a key role in facilitating electron donation and back-donation processes, strengthening adsorption and stabilizing the protective layer formed on the metal surface [10]. In this context, phenolic compounds, which inherently contain aromatic rings and conjugated π -electron systems, are particularly effective corrosion inhibitors, as their electronic structure favors strong interfacial interactions and the formation of stable adsorbed films on metallic surfaces [11].

Consequently, increasing attention has been directed toward naturally derived inhibitors, which combine low cost, wide availability, and a high density of promising functional groups. Plant-based materials, in particular, represent an attractive class of eco-friendly corrosion inhibitors, as they are renewable, biodegradable, and rich in organic molecules containing heteroatoms (O, N, and S), aromatic rings, and conjugated systems capable of adsorbing onto metallic surfaces. According to Hemalatha et al. [12], plant extracts act primarily through adsorption mechanisms that lead to the formation of protective films, effectively isolating the metal surface from aggressive corrosive media. These natural inhibitors offer a sustainable alternative to conventional synthetic compounds, which are often costly and environmentally hazardous, while maintaining high inhibition efficiencies through physicochemical or chemisorption processes.

In this sense, the use of cagaita extract is particularly attractive, since cagaita (*Eugenia dysenterica*) is a native fruit of the Brazilian Cerrado, one of the largest and most biodiverse biomes in the world. This wide natural distribution makes cagaita a readily available and sustainable raw material. Moreover, cagaita fruits are especially rich in phenolic compounds, including gallic, caffeic, vanillic, p-coumaric, syringic, ferulic and salicylic acids, as well as flavonoids such as epicatechin, quercetin and rutin, as extensively reported in the literature. These compounds contain multiple aromatic rings, conjugated π -electron systems and heteroatoms, features that are well known to promote strong adsorption onto metallic surfaces and the formation of protective films. Therefore, the high phenolic content of cagaita extract provides a strong chemical basis for its application as a green and efficient corrosion inhibitor, aligning sustainability, low cost, and corrosion protection efficiency [13,14]. In our previous work, it was demonstrated that the aqueous extract of cagaita is mainly composed of quercetin and Epicatechin [14]. Due to their multiple phenolic hydroxyl groups and conjugated π -electron systems, these flavonoids can be employed as corrosion inhibitors by promoting adsorption onto the metal surface.

In this sense, the use of cagaita extract is particularly attractive, since cagaita (*Eugenia dysenterica*) is a native fruit of the Brazilian Cerrado, one of the largest and most biodiverse biomes, and is widely available. The extract was chemically characterized by spectroscopic techniques, which confirmed the presence of phenolic compounds rich in hydroxyl groups, aromatic rings and conjugated π -electron systems. FTIR analysis revealed characteristic O-H and C=C stretching bands associated with phenolic structures, while UV-Vis spectroscopy evidenced electronic transitions typical of conjugated aromatic systems. These structural

features favor strong adsorption onto metallic surfaces and the formation of protective films, even under highly aggressive acidic conditions. Therefore, the chemical characterization of the cagaita extract supports its application as a low-cost, sustainable and efficient corrosion inhibitor in 10% HCl solution.

2. Experimental

2.1. Preparation of cagaita pulp

Eugenia dysenterica DC fruits (Fig. 2) were obtained in Brazil. Fully ripe fruits were collected in Sete Lagoas, Minas Gerais State, Brazil (19°28'36" S, 44°11'43" W) during 2024 and transported to the Chemistry Laboratory of the Federal University of São João del-Rei (UFSJ). The harvesting of *Eugenia dysenterica* DC fruits was conducted in accordance with Brazilian Law No. 12,727, dated October 17, 2012, which regulates the protection of native vegetation. The fruits were collected from native (wild) plants occurring in cerrado areas of the UFSJ campus.

Permission for plant collection was granted by the responsible institutional authority of the Federal University of São João del-Rei (UFSJ), as the collection was carried out on public land for non-commercial scientific research purposes, in compliance with Brazilian Law No. 12,651/2012 and Law No. 13,123/2015. Under these conditions, no specific governmental license was required for the collection of non-timber forest products.

The plant species was taxonomically identified by Prof. Dr. Julio Onésio Ferreira Melo (Federal University of São João del-Rei, UFSJ), and a voucher specimen was deposited in the Herbário PAMG (Empresa de Pesquisa Agropecuária de Minas

Gerais – EPAMIG), Belo Horizonte, Minas Gerais, Brazil, under voucher number PAMG 59803.

The pulp was manually separated from the seeds, cleaned, and thoroughly washed with deionized water. The biomass then underwent a simple and efficient preparation process designed to minimize energy and resource consumption. High-purity water, obtained using a Quimis deionization system, was used in the preparation of all solutions to ensure consistency and purity. The pulp was ground using a knife mill to obtain a homogeneous material suitable for subsequent use (Fig. 2). This preparation route required no chemical treatments or high-energy inputs, such as thermal activation or specialized surface modifications.

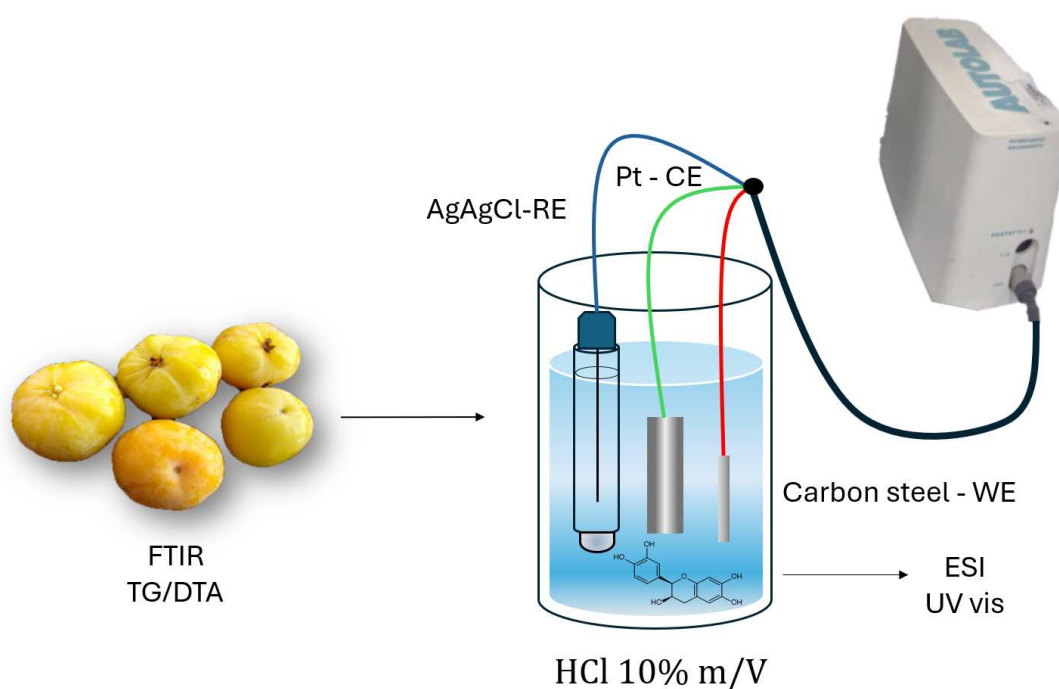


Figure 2. Schematic illustration of the corrosion testing system in 10 wt% HCl with increasing concentrations of cagaita pulp extract. The concentration-dependent

inhibition behavior was evaluated using electrochemical measurements in a three-electrode configuration.

2.2. Cagaita pulp characterization

Fourier-transform infrared spectroscopy (FTIR/ATR) analyses of the biomass were performed using an Agilent Cary 630 FTIR spectrophotometer (Agilent Technologies, USA) equipped with an attenuated total reflection (ATR) accessory.

Thermal analysis was carried out at the Chemistry Department Laboratory of the Federal University of Minas Gerais (UFMG) using Mettler thermal analysis equipment. Approximately 40 mg of the biomass sample were placed in an aluminum crucible and heated from 25 to 800 °C at a heating rate of 10 °C·min⁻¹ under a synthetic air atmosphere with a flow rate of 50 mL·min⁻¹.

The pulp extract was analyzed by electrospray ionization mass spectrometry (ESI-MS) using an Agilent ion trap mass spectrometer. UV-Vis absorption spectra of the pulp extract were recorded in scan mode using a FEMTO 800XI UV-Vis spectrophotometer.

2.3. Electrochemical measurements

The electrolyte solution was prepared using 10% (v/v) HCl, and the cagaita pulp extract was employed as a corrosion inhibitor at different mass additions. Electrochemical measurements were performed using a three-electrode electrochemical cell connected to an AUTOLAB PGSTAT 30 potentiostat/galvanostat. A platinum electrode was used as the counter (auxiliary) electrode, while a saturated

Ag/AgCl electrode served as the reference electrode. The working electrode consisted of carbon steel, with an exposed area of 1 cm². Prior to each measurement, the working electrode surface was mechanically polished using 600-grit sandpaper, rinsed thoroughly with distilled water, and dried. All electrochemical experiments were conducted at 25 °C, without solution agitation, in order to ensure stable and reproducible conditions. Potentiodynamic polarization measurements were carried out using linear polarization, with a scan rate of 1 mV·s⁻¹, selected to minimize capacitive current contributions and to ensure reliable determination of corrosion parameters [15].

2.3.1 Tafel analysis

The anodic and cathodic branches of the potentiodynamic polarization curves were analyzed within the Tafel approximation, which assumes an exponential dependence between the electrode overpotential and the current density in the activation-controlled regime. Under these conditions, the polarization behavior can be described by a linear relationship between the overpotential and the logarithm of the current density. Accordingly, the anodic and cathodic branches were interpreted using the Tafel relationship, as expressed in Eqs. (1) and (2) [16].

$$\eta = E - E_{corr} (V) \quad (\text{Eq. 1})$$

$$\eta = a + b \log i \quad (\text{Eq. 2})$$

where:

- E = applied potential (V vs reference)

- E_{corr} = corrosion potential (V vs reference)
- η = overpotential (V)
- i = current density ($\text{A} \cdot \text{cm}^{-2}$) (or $\text{mA} \cdot \text{cm}^{-2}$, depending on the instrument output)
- a = intercept term (V), dependent on the logarithmic base and current units
- b = Tafel slope ($\text{V} \cdot \text{dec}^{-1}$), reported as:
 - b_a anodic Tafel slope ($\text{V} \cdot \text{dec}^{-1}$)
 - b_c cathodic Tafel slope ($\text{V} \cdot \text{dec}^{-1}$)

From Tafel extrapolation, the corrosion current density (i_{corr} , $\text{A} \cdot \text{cm}^{-2}$ or $\text{mA} \cdot \text{cm}^{-2}$) was obtained by extrapolating the linear regions of the anodic and cathodic polarization branches to the corrosion potential (E_{corr}). This parameter provides a quantitative measure of corrosion kinetics and reflects changes in electrochemically active surface area induced by inhibitor adsorption. The corrosion rate (CR, $\text{mm} \cdot \text{year}^{-1}$) was calculated from i_{corr} using standard electrochemical conversions based on the metal equivalent weight and density [7-9,16].

a) Inhibition efficiency

Using corrosion current density, the inhibition efficiency was calculated based on the reduction of the corrosion current density induced by the presence of the inhibitor. This approach assumes that the decrease in i_{corr} reflects the extent to which the electrochemically active surface area is blocked by adsorbed inhibitor

species. The inhibition efficiency (η , %) was determined as Eq.3 or alternatively, using corrosion rate values (Eq.4):

$$\eta(\%) = \frac{i_{\text{corr},0} - i_{\text{corr}}}{i_{\text{corr},0}} \times 100 \quad (\text{Eq. 3})$$

$$\eta(\%) = \frac{\text{CR}_0 - \text{CR}}{\text{CR}_0} \times 100 \quad (\text{Eq. 4})$$

where:

- $\eta(\%)$ = inhibition efficiency (%)
- $i_{\text{corr},0}$ = corrosion current density in the uninhibited solution ($\text{A} \cdot \text{cm}^{-2}$)
- i_{corr} = corrosion current density in the presence of inhibitor ($\text{A} \cdot \text{cm}^{-2}$)
- CR_0 = corrosion rate in the blank solution ($\text{mm} \cdot \text{year}^{-1}$)
- CR = corrosion rate in the presence of inhibitor ($\text{mm} \cdot \text{year}^{-1}$)

The use of inhibition efficiency derived from electrochemical parameters is well established in corrosion inhibition studies involving plant extracts and biomass-derived inhibitors [7-9,16].

b) Adsorption isotherm models

Assuming that the inhibition efficiency reflects the fraction of active surface sites blocked by adsorbed inhibitor species, the surface coverage (θ) was estimated according to Eq. (5), where θ represents the surface coverage (dimensionless, 0–1):

$$\theta = \frac{i_{\text{corr},0} - i_{\text{corr}}}{i_{\text{corr},0}} \text{ or } \theta = \frac{\text{CR}_0 - \text{CR}}{\text{CR}_0} \quad (\text{Eq. 5})$$

This approach is widely used to relate electrochemical measurements to adsorption models in corrosion inhibition systems based on natural extracts, where adsorption is assumed to be the primary inhibition mechanism [7-9]. Since θ is dimensionless, the units of the isotherm constants depend on the concentration unit adopted (here, $\text{g} \cdot \text{L}^{-1}$). This convention is commonly used in adsorption studies involving complex biomass-derived inhibitors [7-9].

- **Langmuir isotherm**

The Langmuir model (Eq. 6) assumes monolayer adsorption on a finite number of identical sites and has been extensively applied to describe the adsorption of organic inhibitors on metallic surfaces [7-9].

$$\theta = \frac{K_L C}{1 + K_L C} \quad (\text{Eq. 6})$$

where:

- K_L = Langmuir adsorption constant ($\text{L} \cdot \text{g}^{-1}$)

- C = inhibitor concentration ($\text{g} \cdot \text{L}^{-1}$)
- θ = dimensionless surface coverage

- **Temkin isotherm**

The Temkin model (Eq. 7) accounts for lateral interactions between adsorbed species and has been successfully employed to describe adsorption processes on heterogeneous surfaces, including biomass-based inhibitor systems [7-9].

$$\theta = \frac{1}{B} \ln (AC) \quad (\text{Eq. 7})$$

where:

- B = Temkin constant (dimensionless), related to adsorbate-adsorbate interactions
- A = Temkin equilibrium binding constant ($\text{L} \cdot \text{g}^{-1}$), such that AC is dimensionless

- **Freundlich isotherm**

The Freundlich isotherm (Eq. 8) is particularly suitable for complex and heterogeneous inhibitor systems, such as plant extracts and lignocellulosic biomaterials, where multiple adsorption sites and interaction energies coexist [7-9]. The prepared pulp was used as a corrosion inhibitor at different mass additions in a 10% (v/v) HCl solution.

$$\theta = K_F C^{1/n} \quad (Eq. 8)$$

where:

- n = heterogeneity parameter (dimensionless)
- is the Freundlich adsorption constant, whose units depend on the value of n . For C expressed in $\text{g} \cdot \text{L}^{-1}$, the units of K_F are $\text{L}^{1/n} \text{g}^{-1/n}$.

3. Results and discussion

3.1 FTIR and thermal analysis of cagaita pulp

Although the corrosion inhibition experiments were carried out using the biomass extract, the characterization of the solid cagaita pulp by FTIR and thermal analysis (TG/DSC) is justified, as it provides essential information on the chemical nature and stability of the compounds that are potentially released into the extract. Plant extracts originate from the solubilization of functional groups and molecular fragments initially embedded in the solid biomass matrix; therefore, the identification of hydroxyl, carbonyl, aromatic, and ether functionalities in the solid material reflects the structural features of the extractable species.

3.1.1 FTIR

Figure 3 presents the FTIR spectra of cagaita pulp and washed cagaita pulp, highlighting the main functional groups associated with phenolic compounds and

biomass constituents. The broad absorption band centered at $\sim 3325\text{ cm}^{-1}$ is assigned to O–H stretching vibrations of hydroxyl groups from phenolic compounds, alcohols, and carboxylic acids, as well as hydrogen-bonded water molecules [17,18]. The bands located at 2920 and 2848 cm^{-1} correspond to the asymmetric and symmetric C–H stretching vibrations of aliphatic $-\text{CH}_2$ and $-\text{CH}_3$ groups [20].

The absorption band observed at 1726 cm^{-1} is assigned to C=O stretching vibrations of carboxylic acid and ester groups, commonly associated with oxygenated functionalities present in polyphenolic components [19,21]. The band at 1624 cm^{-1} is attributed to C=C stretching vibrations of phenyl rings, which are abundant in polyphenolic components of plant-derived materials [21]. The signal at 1450 cm^{-1} is associated with C–H bending vibrations and contributions from aromatic skeletal modes, further supporting the presence of substituted aromatic compounds [21]. Bands observed at 1158 and 1014 cm^{-1} are assigned to C–O and C–O–C stretching vibrations, characteristic of polysaccharides and phenolic conjugates commonly found in plant-derived biomaterials, which may include glycosylated phenolic structures [22].

The band observed at $\sim 817\text{ cm}^{-1}$ can be attributed to α -glycosidic bonds, which are characteristic of polysaccharide structures commonly found in plant-derived biomaterials [23].

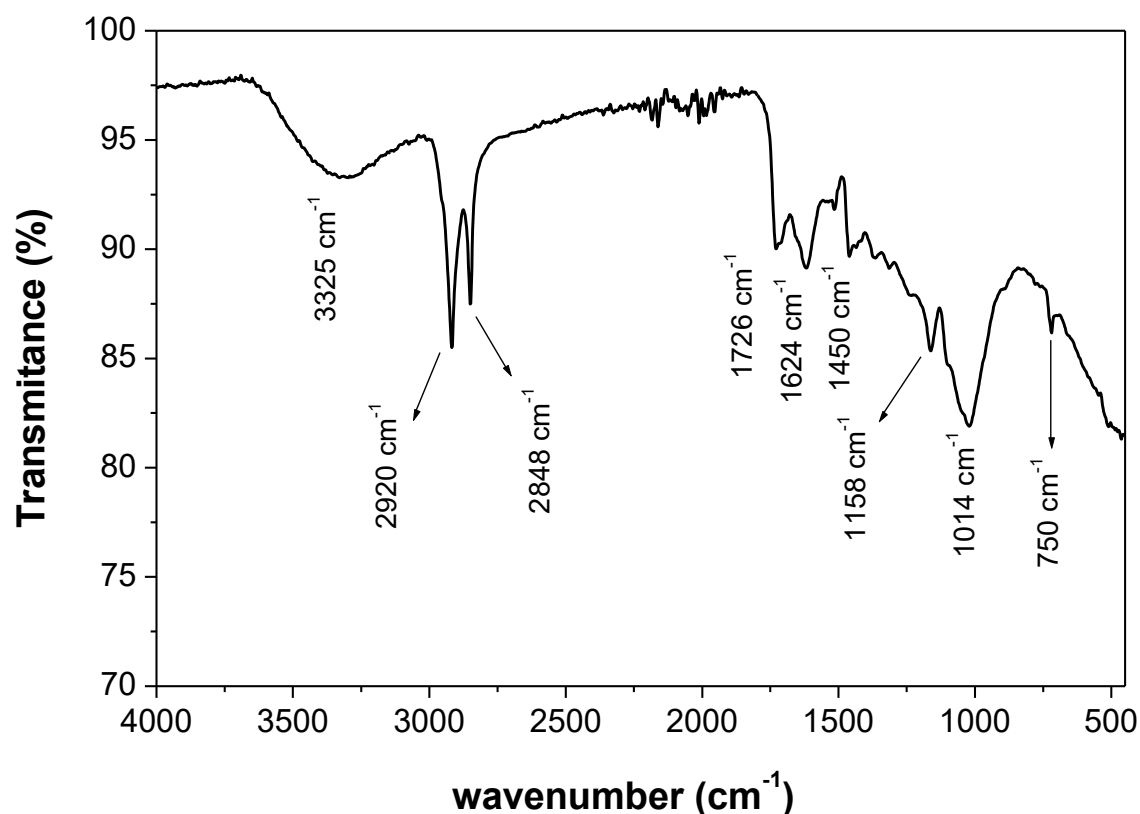


Figure 3 - FTIR spectrum of *cagaita* pulp.

3.1.2 Thermal analysis

Figure 4 shows the thermogravimetric (TG) and differential thermal analysis (DTA) curves of *cagaita* pulp recorded under a synthetic air atmosphere. A pronounced initial mass loss occurring below 100–140 °C is observed, which is attributed to the removal of free and weakly bound water, as well as other volatile components, as commonly reported in thermogravimetric analyses of fruit-derived biomaterials [24]. This dehydration process is accompanied by a strong endothermic event in the DTA curve, confirming the predominance of moisture evaporation in this temperature range. In contrast to studies performed on dried

fruit residues, the much higher mass loss observed in the present work reflects the intrinsically high moisture content of the fresh cagaita pulp, indicating that dehydration phenomena dominate its thermal behavior.

At higher temperatures, a weak exothermic feature is observed in the DTA curve, appearing as a small peak around 450–520 °C. This event is attributed to the oxidation of residual organic matter, including carbonaceous fragments derived from carbohydrate-rich components that remain after the extensive dehydration stage [24]. The low intensity of this signal indicates that only a minor fraction of thermally stable organic material persists, confirming that the thermal behavior of the fresh cagaita pulp is predominantly governed by moisture removal rather than by extensive organic degradation [25].

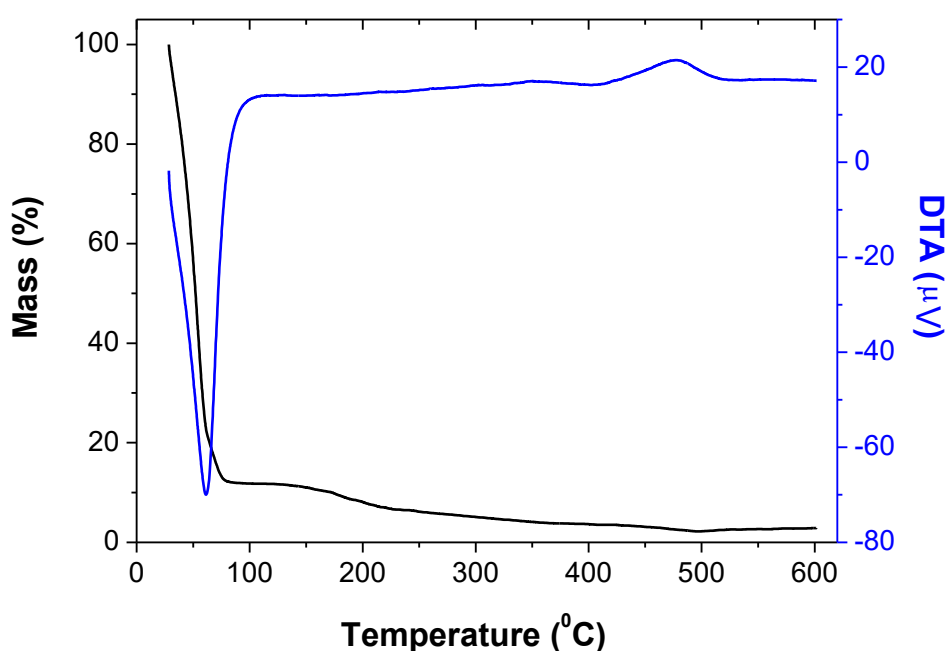


Figure 4- Thermogravimetric (TG) and differential thermal analysis (DTA) curves of cagaita pulp recorded under synthetic air atmosphere.

3.2 ESI-MS and UV-Vis analysis of the extract

3.2.1 ESI-MS analysis

Electrospray ionization mass spectrometry (ESI-MS) was employed to obtain molecular-level information on the chemical composition of the extract (Fig. 5). The ESI mass spectrum exhibits several ions in the low- and mid- m/z range, which are consistent with the presence of phenolic acids and their conjugated derivatives, commonly reported in plant-derived matrices [27]. Negative ionization mode was selected for ESI-MS analysis because it allows the detection of a broader range of phenolic acids and organic acid derivatives in plant matrices, whereas positive ionization typically yields fewer detectable phenolic species, as reported in the literature [27].

According to the literature, among the various phenolic compounds identified in the extract—such as caftaric acid, p-coumaric acid, and related derivatives—the predominant constituents are epicatechin and quercetin [14]. Figure 5 shows the negative-ion ESI mass spectrum of the extract, in which the ion at m/z 301 is clearly observed and assigned to quercetin [28]. A magnified view of the MS/MS spectrum of the ion at m/z 289 reveals characteristic fragment ions that are exclusively consistent with the fragmentation pattern of epicatechin, confirming its presence in the extract.

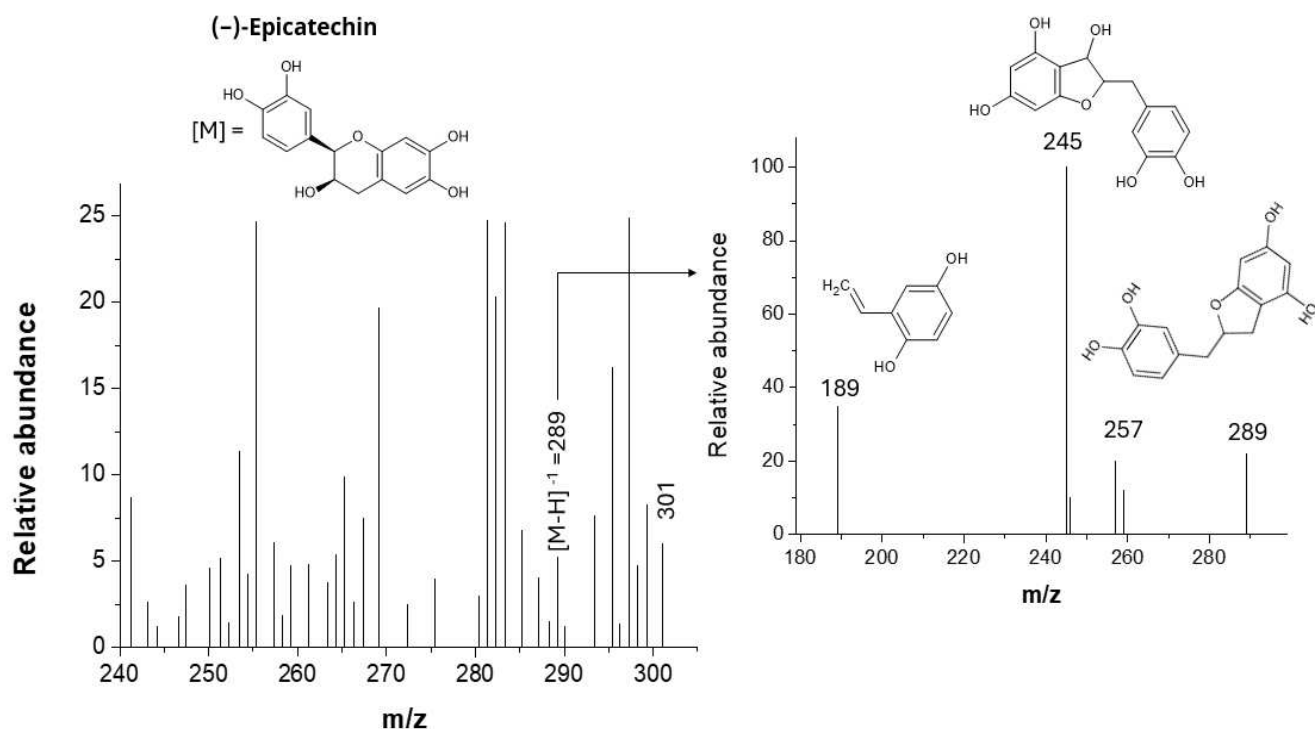


Figure 5- Negative-ion ESI mass spectrum of the extract highlighting the main phenolic constituents.

3.2.2 UV-Vis spectroscopy

The UV-Vis spectrum of the extract shows intense absorption in the ultraviolet region, with a pronounced maximum at approximately 275 nm, followed by a broad absorption band extending from about 250 to 320 nm (Fig. 6). This spectral profile is characteristic of phenolic-rich plant extracts, in which multiple aromatic chromophores, associated with conjugated π -electron systems, contribute simultaneously to the overall absorption [31].

According to Guemari et al. [31], UV-Vis spectrophotometry applied to natural extracts enables the assessment of phenolic compound classes rather than the identification of individual molecular species, since the observed absorption

bands arise from the collective contribution of structurally related phenolics [53]. In particular, absorption bands in the 270–280 nm range are commonly associated with $\pi \rightarrow \pi$ electronic transitions of aromatic phenolic systems, which are frequently reported for phenolic acids, including hydroxybenzoic and hydroxycinnamic derivatives

The interpretation of the UV–Vis data is further supported by spectroscopic studies of model phenolic compounds. Using p-coumaric acid as a representative hydroxycinnamic acid, Cunha et al. [32] showed that the UV–Vis absorption of these compounds depends strongly on their protonation state, leading to shifts in band position and band broadening associated with changes in electronic delocalization. Similar behavior has been reported for flavonoids such as quercetin, whose UV–Vis spectra display broad, environment-sensitive absorption bands arising from $\pi \rightarrow \pi$ transitions in aromatic rings and conjugated systems, and which are markedly influenced by solvent effects and intermolecular interactions [33]. These observations indicate that broad UV–Vis features in plant extracts may originate not only from molecular diversity but also from the intrinsic electronic response of individual phenolic compounds.

Therefore, in a multicomponent system such as a plant extract—where free phenolic acids, conjugated derivatives, and different acid–base forms coexist—the superposition of individual spectral contributions naturally results in broad and overlapping UV absorption bands, as observed in the present spectrum. Consequently, the UV–Vis data confirm the presence of aromatic phenolic

chromophores, but do not allow unambiguous molecular identification.

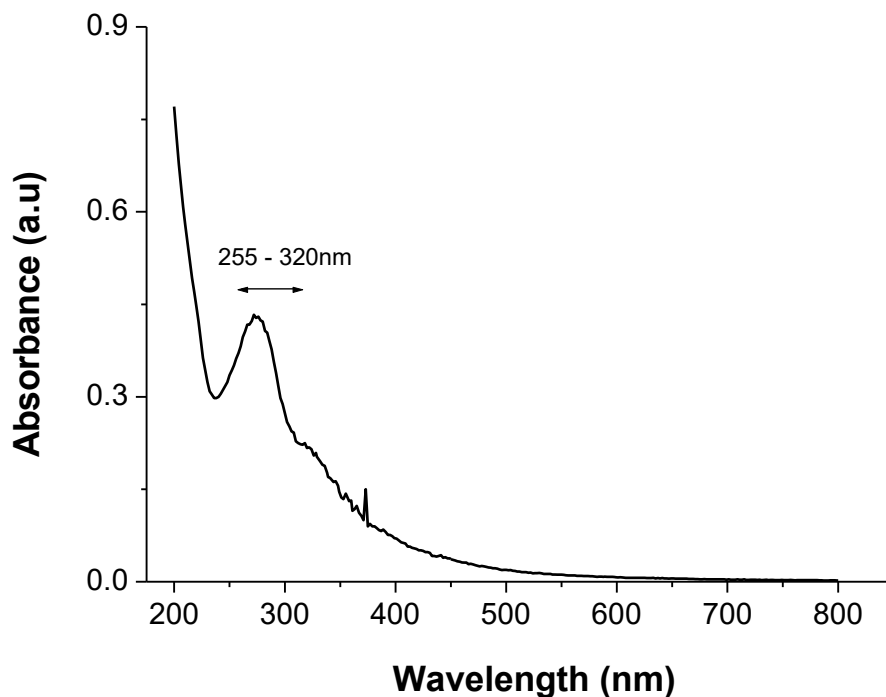


Figure 6- UV-Vis absorption spectrum of the cagaita extract, showing intense absorption in the 22round22oleta region with a maximum 22round 275 nm and a broad band extending from approximately 255 to 320 nm, characteristic of phenolic-rich plant extracts.

3.3 Electrochemical characterization

Potentiodynamic polarization curves of carbon steel in 10 wt% HCl solution without inhibitor (red curve) and with 0.3 g L⁻¹ of cagaita extract (black curve), showing a reduction in current density in the presence of the extract. The data were fitted using the Butler-Volmer equation (Fig. 7) [15]. The electrochemical parameters obtained are summarized in Table 1.

In acidic media, the corrosion of carbon steel proceeds through the anodic dissolution of iron ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) coupled with the cathodic reduction of hydrogen ions ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). The addition of cagaita extract results in a pronounced decrease in the corrosion current density, which drops from 8.51×10^{-4} to $0.68 \times 10^{-4} \text{ A.cm}^{-2}$. This substantial reduction in i_{corr} indicates a significant decrease in the overall corrosion rate and corresponds to an inhibition efficiency of approximately 92%, confirming the effective protective action of the extract.

In parallel, noticeable changes are observed in the kinetic parameters derived from Tafel analysis. The anodic Tafel slope decreases from 123 to 99 $\text{mV} \cdot \text{dec}^{-1}$, while the cathodic Tafel slope decreases from 193 to 124 $\text{mV} \cdot \text{dec}^{-1}$ upon inhibitor addition. These variations indicate that the presence of the extract alters the charge-transfer kinetics of both anodic iron dissolution and cathodic hydrogen evolution reactions. The simultaneous modification of both slopes suggests that the inhibitor affects both electrochemical processes rather than selectively influencing only one.

Consistent with these changes, the transfer coefficient (α), which is related to the symmetry of the activation barrier according to the Tafel relationship $\beta = \frac{2.303RT}{\alpha nF}$, decreases slightly from 0.612 to 0.56 in the inhibited system. This modest variation in α indicates that, although the overall reaction mechanism remains unchanged, the energy barrier for electron transfer is modified by the adsorption of inhibitor molecules on the steel surface.

In contrast, only a minor shift in the corrosion potential is observed, from -0.4487 to -0.4419 V , indicating that the thermodynamic equilibrium of the metal/solution interface is essentially preserved. Taken together, the strong reduction in corrosion current density, the changes in Tafel slopes and transfer

coefficient, and the small displacement of the corrosion potential demonstrate that the cagaita extract behaves as a mixed-type corrosion inhibitor. Its protective action is governed predominantly by adsorption-controlled surface blocking, which suppresses both anodic and cathodic reactions without inducing significant redox-driven shifts in the corrosion potential.

Anticorrosive applications of epicatechin [34] and quercetin [35] have been reported in the literature. The HOMO and LUMO energy values and the corresponding band gaps (ΔE), summarized in Table 2, are consistent with their corrosion inhibition properties. In acidic media, both molecules tend to exhibit reduced band gap values, which are commonly associated with enhanced molecular reactivity and adsorption onto the metal surface, with epicatechin showing a pronounced sensitivity to protonation state [34].

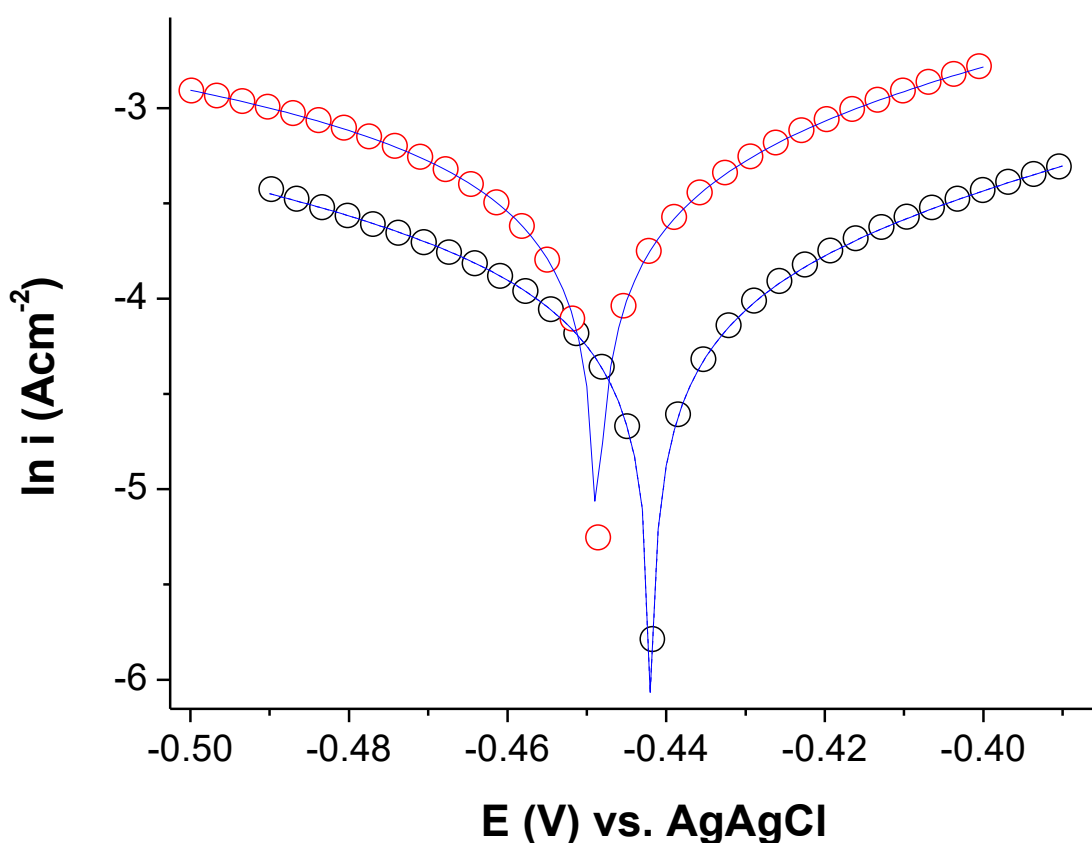


Figure 7- Potentiodynamic polarization curves of carbon steel in 10 wt% HCl solution without inhibitor (red curve) and with 0.3 g L⁻¹ of cagaita extract (black curve), showing a reduction in current density in the presence of the extract.

Table 1. Electrochemical parameters obtained from Tafel polarization curves for carbon steel in 10 wt% HCl solution in the absence and presence of cagaita extract (0.3 g L⁻¹).

System	E V	i _{corr} A·cm ⁻²	β _a mV·dec ⁻¹	β _c mV·dec ⁻¹	α	η %
Blank (10 wt% HCl)	-0.4487	8.51x 10 ⁻⁴	123	193	0.612	—
10 wt% HCl + cagaita extract	-0.4419	0.68 x10 ⁻⁴	99	124	0.56	80.3

Table 2. Frontier molecular orbital energies (E_{HOMO} and E_{LUMO}) and band gap values (ΔE) of epicatechin and quercetin in neutral and protonated states, as reported in the literature.

Compound	State	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Reference
Epicatechin	Neutral	-5.80	-1.18	4.61	[34]
	Protonated	-6.03	-5.37	0.66	
Quercetin	Neutral	-5.30	-1.90	3.40	[35]
	Protonated	-5.7 to -6.0	-2.5 to -3.0	~ 2	

3.4 Adsorption isotherm

Figure 8 shows the relationship between surface coverage (θ) and cagaita pulp concentration. The experimental data were fitted using three adsorption isotherm models, namely Langmuir, Freundlich, and Temkin. The corresponding adsorption parameters and statistical indicators are summarized in Table 3.

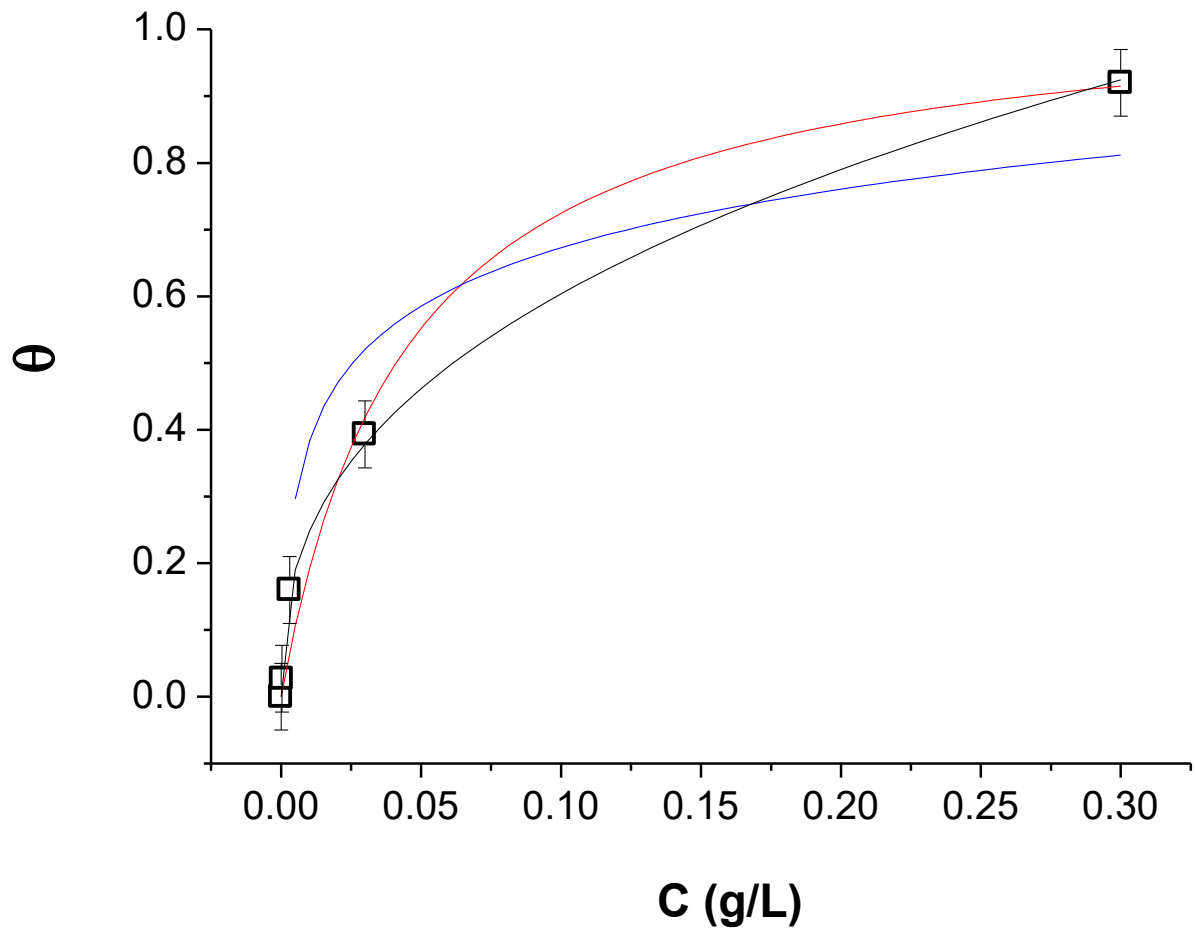


Figure 8- Surface coverage (θ) as a function of inhibitor concentration (C) for carbon steel in 10 wt% HCl. Experimental data (symbols) and fitted adsorption isotherm models (solid lines).

Table 3. Adsorption isotherm parameters obtained from Langmuir, Freundlich, and Temkin models for the cagaita extract on carbon steel in 10 wt% HCl.

Isotherm model	Parameter	Value	Standard error	R ²	χ^2
Langmuir	K_L	21.99	6.88	0.9825	0.00336
	$L \cdot g^{-1}$				
	θ_{max}	1.05	0.09		
Freundlich	K_F	1.47	0.06	0.9973	0.00053
	n	2.58	0.14		
Temkin	A	2044.8	1763.3	0.9124	0.02035
	B	0.126	0.028		

The surface coverage (θ) increased progressively with the concentration of the cagaita pulp extract and approached a plateau at higher concentrations, indicating saturation of the metal surface and supporting an adsorption-controlled inhibition mechanism. To gain insight into the adsorption behavior, the experimental data were fitted to Langmuir, Freundlich, and Temkin isotherm models (Fig.8). Among the tested models, the Freundlich isotherm provided the best statistical agreement ($R^2 = 0.9973$; $\chi^2 = 0.00053$), suggesting a heterogeneous metal surface and non-ideal adsorption behavior, which is consistent with the complex chemical composition of natural extracts. Nevertheless, the Langmuir model also adequately described the experimental trend ($R^2 = 0.9825$), yielding a high affinity constant

($K_L = 21.99 \text{ L}\cdot\text{g}^{-1}$) and a maximum surface coverage close to unity ($\theta_{\text{max}} \approx 1$). This behavior is indicative of progressive blocking of active corrosion sites and the formation of a protective adsorbed film on the steel surface.

The standard free energy of adsorption was estimated from the Langmuir adsorption constant using $\Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K_{\text{ads}})$. After converting K_L obtained with concentration in $\text{g}\cdot\text{L}^{-1}$ to K_{ads} in $\text{L}\cdot\text{mol}^{-1}$ using epicatechin as a representative molecule, $\Delta G_{\text{ads}}^{\circ}$ was found to be approximately $-31.6 \text{ kJ}\cdot\text{mol}^{-1}$ at 298 K, indicating strong adsorption with mixed physisorption/chemisorption contributions.

Figure 9 shows the Arrhenius plots ($\ln \text{CR}$ vs. $1/T$) for carbon steel in 10 wt% HCl solution in the absence and presence of cagaita pulp extract ($0.3 \text{ g}\cdot\text{L}^{-1}$). A clear linear behavior is observed in both cases, indicating that the corrosion process follows Arrhenius-type temperature dependence over the investigated temperature range

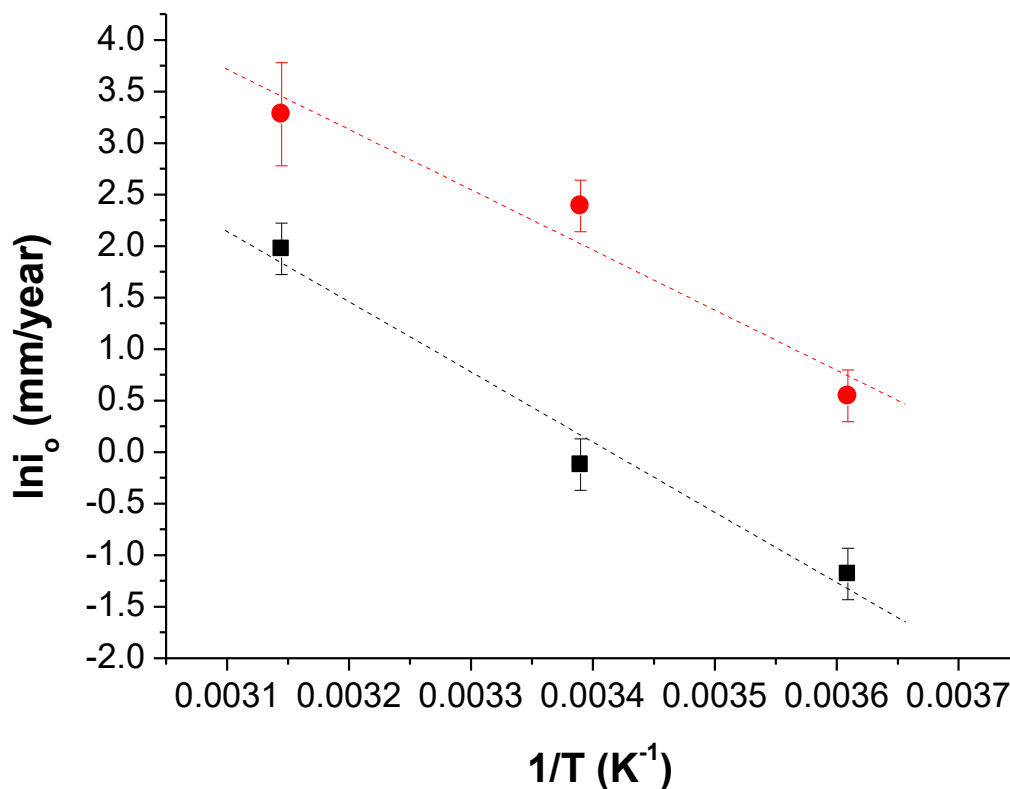


Figura 9- Arrhenius plots for the corrosion rate of carbon steel in 10 wt% HCl solution in the absence (black squares) and presence (red circles) of cagaita pulp extract (0.3 g·L⁻¹).

Arrhenius plots of the corrosion rate revealed a linear dependence of $\ln i_0$ on $1/T$ for both systems, indicating thermally activated processes. The apparent activation energy decreased slightly from 53.8 kJ·mol⁻¹ for the blank solution to 48.6 kJ·mol⁻¹ in the presence of the cagaita extract. This behavior suggests that the inhibitor alters the corrosion mechanism through surface adsorption and film formation, rather than acting solely as a physical barrier. Similar values of the pre-exponential factor further indicate that the inhibition effect is mainly associated

with a reduction in the number of active corrosion sites rather than a change in the frequency of elementary corrosion events.

Table 4. Arrhenius parameters ($\ln A$ and activation energy, E_a) for carbon steel corrosion in 10 wt% HCl in the absence and presence of cagaita extract.

System	$\ln A$	E_a (kJ·mol ⁻¹)	R^2
Blank (10 wt% HCl)	23.19	53.8	0.97
10 wt% HCl + cagaita extract (0.3 g·L ⁻¹)	23.26	48.6	0.98

4 Conclusion

The aqueous extract of cagaita (*Eugenia dysenterica*) proved to be an effective and environmentally friendly corrosion inhibitor for carbon steel in 10 wt% HCl. The corrosion current density decreased from 8.51×10^{-4} to 0.68×10^{-4} A·cm⁻² in the presence of 0.3 g·L⁻¹ of extract, corresponding to an inhibition efficiency of 80–92%. The small corrosion potential shift ($\Delta E_{\text{corr}} \approx 7$ mV), together with reductions in anodic ($123 \rightarrow 99$ mV·dec⁻¹) and cathodic ($193 \rightarrow 124$ mV·dec⁻¹) Tafel slopes, confirms a mixed-type inhibition mechanism dominated by surface adsorption.

Adsorption studies showed increasing surface coverage with inhibitor concentration, with the Freundlich model providing the best fit ($R^2 = 0.9973$; $\chi^2 = 0.00053$), while the Langmuir model also described the data well ($R^2 = 0.9825$),

yielding $K_L = 21.99 \text{ L}\cdot\text{g}^{-1}$ and $\theta_{\max} \approx 1.05$. The estimated standard free energy of adsorption ($\Delta G^\circ_{\text{ads}} \approx -31.6 \text{ kJ}\cdot\text{mol}^{-1}$) indicates strong adsorption involving both physisorption and chemisorption.

Arrhenius analysis revealed a decrease in activation energy from 53.8 to 48.6 $\text{kJ}\cdot\text{mol}^{-1}$ in the presence of the extract, indicating inhibition through surface site blocking rather than a change in the intrinsic corrosion mechanism. Spectroscopic analyses confirmed the presence of phenolic compounds, mainly epicatechin and quercetin, whose HOMO–LUMO characteristics reported in the literature support their adsorption and corrosion inhibition performance under acidic conditions.

DATA AVAILABILITY STATEMENT : The authors declare that the data supporting the findings of this study are available within the paper.

INTEREST STATEMENT : The authors declare that they have no conflict of interest

FUNDING DECLARATION : The authors declare that they were not funded by any organization or fund.

AUTHOR CONTRIBUTION: E.M.G. conceived and designed the study, performed the experiments, and contributed to the kinetic analysis. H.A.T. and J.O.F.M wrote the main manuscript text and prepared the figures. All authors discussed the results, reviewed the manuscript, and approved the final version for submission.

CONSENT TO PUBLISH DECLARATION: Not applicable.

CONSENT TO PARTICIPATE DECLARATION: Not applicable.

Ethics declaration: Not applicable.

Acknowledgements

We are grateful to CNPq for financial support. This work is a collaboration research project of Rede Mineira de Química (RQ-MG). We are also grateful to Department of Natural Sciences/UFSJ

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