Assessment of *Eichhornia crassipes* as a Green Corrosion Inhibitor for AISI 1005 Steel in Acidic Environments

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Green corrosion inhibitors have shown considerable promise as a viable alternative to synthetic inhibitors for preventing corrosion in various applications. In this study, the aquatic plant *Eichhornia crassipes* (water hyacinth), native to the Pantanal region, was evaluated for its potential as a green corrosion inhibitor for AISI 1005 steel in an electrolyte containing 0.01 mol L^{-1} HCl. The plant extraction was conducted using both maceration and ultrasound with the electrolyte. The study employed open circuit potential (OCP), potentiodynamic polarization (PDP) using electrochemical techniques, and weight loss (WL) tests were performed. The results indicated a reduction in the rate of corrosive reactions on the steel surface, particularly in cathodic reactions, with corrosion inhibition efficiency reaching nearly 90 %.

Keywords
green corrosion inhibitors, *Eichhornia crassipes*, AISI 1005 steel corrosion

Introduction

Corrosion is a widespread issue affecting sectors such as chemical, oil, petrochemical, shipbuilding, civil construction, transportation, and even the arts, such as monuments and sculptures[1,2]. The process of corrosion involves the degradation of materials, especially metals, due to chemical or electrochemical reactions, often with mechanical strain[1,3–5]. Steel, widely used in industrial applications for its mechanical properties and chemical versatility, is particularly vulnerable to corrosion[6]. Globally, around 30 % of iron and steel production is lost to corrosion, significantly impacting countries' GDP, ranging from 1 % to 5 % [1,7]. In 2019, Brazil's corrosion-related losses were estimated at about 4 % of GDP, approximately $290 billion[7].

Understanding corrosion mechanisms and implementing effective measures to protect steel is crucial. Corrosion inhibitors have emerged as promising solutions. These substances, when used in appropriate concentrations, can delay or inhibit corrosive processes[6,7]. Organic inhibitors, also known as adsorption inhibitors, protect by adsorbing onto the metal surface and forming a protective film. This film hinders dissolution and reduction reactions, mitigating both anodic and cathodic processes, and disrupting electrochemical action[8].

Concerns about the use of synthetic inhibitors include their toxicity, ecological impact, and environmental harm. Rising environmental awareness has increased interest in non-toxic organic inhibitors[9–11]. These inhibitors are typically composed of low-cost, environmentally acceptable compounds that do not threaten ecosystems. Consequently, green inhibitors derived from natural extracts have gained considerable attention as environmentally friendly alternatives for corrosion protection[12].

Green corrosion inhibitors derived from natural extracts provide several benefits over traditional synthetic inhibitors. Environmentally, they are considered greener due to their renewable sources and biodegradability, reducing ecosystem impact. Their production requires less energy and produces fewer hazardous byproducts, promoting sustainable corrosion control practices[12]. Natural extracts generally exhibit lower toxicity levels, making them safer for human health and the environment[1,13]. Economically, they are advantageous due to their abundance, availability, and cost-effectiveness compared to synthetic alternatives. Additionally, using locally sourced natural extracts supports local industries and contributes to sustainable development[7].

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Natural extracts have shown promising efficiency as corrosion inhibitors by forming protective barriers on metal surfaces and reducing corrosion rates. Their efficacy is attributed to various compounds, including alkaloids, phenolic compounds, flavonoids, and organic acids. One such extract of interest comes from *Eichhornia crassipes*, known as water hyacinth. This invasive aquatic plant, native to South America, has spread globally and is considered a problematic weed due to its rapid reproduction and dense mat formation on water surfaces[14–16].

Shanab *et al.*[17] reported characterizing various fractions of *Eichhornia crassipes* extract. These fractions contained alkaloids, carotenoids, phenolic compounds, and terpenoids, and exhibited antioxidant activity. Similarly, Bharati *et al.*[18] identified saponins, tannins, anthocyanins, sterols, glycosides, flavonoids, and anthraquinones present in water hyacinth. The chemical composition of water hyacinth itself includes organic compounds[19–21] with potential corrosion inhibition properties. These molecules include tannins, phenols, anthraquinones, cellulose, lignin and proteins. They are characterized by a high content of carbon and oxygen in their molecular structure and show antioxidant activity. These latter compounds are believed to contribute to the plant's corrosion inhibition capabilities by adsorbing onto metal surfaces and forming a protective film[1,19,21,22]. Mohamed *et al.*[1] investigated the inhibition efficiency of water hyacinth extract obtained by alcoholic extraction of steel in an acidic medium, achieving a maximum inhibition efficiency of 89 %.

Omoruwou, Okewale and Owabor[23] conducted a statistical analysis to optimize the corrosion inhibition properties of water hyacinth extract on mild steel in an acidic environment. The presence of alkaloids, saponins, terpenoids, and aromatic rings in water hyacinth is believed to enhance the corrosion inhibition process on the mild steel surface. These molecules likely form a protective film on the metal surface, thereby hindering both the dissolution of the mild steel (anodic reaction) and the evolution of hydrogen gas (cathodic reaction).

Other authors have explored the inhibition properties of extracts obtained from different parts of water hyacinth. Oloruntoba *et al.*[24] investigated the use of an extract obtained exclusively from the roots. The authors show the presence of O–H, C–H, C=C, C–N, and O–H vibrations, all important in the inhibitory properties of the extract. Additionally, phytochemical screening evidenced the presence of saponin (19 mg mL^{-1}), tannin (3.4 mg mL^{-1}), terpenoid (6.8 mg mL^{-1}), cardiac glycoside (12.3 mg mL^{-1}), and flavonoid (6.3 mg mL^{-1}) in the extract. The addition of this extract provided a corrosion inhibition efficiency of around 70 % for steel in 0.5 mol L^{-1} H_2SO_4. Saja Ahmed Abd-Alkareem[25] obtained an extract of the roots via absolute methanol extraction, and achieved an efficiency of 93 % for steel in a 1 mol L^{-1} HCl solution with 500 ppm of extract.

Extracts obtained from the leaves of water hyacinth have also been tested as a corrosion inhibitor for steel. Kavitha and Manjula[26] investigated the synergistic effect of *Eichhornia crassipes* leaf extract and Zn^{2+} ions as a corrosion inhibitor for mild steel at different temperatures in a neutral aqueous medium containing sodium chloride (NaCl). Their results demonstrated that the combination of the extract with Zn^{2+} exhibited a corrosion inhibition efficiency ranging from 25 % to 75 %.

Ulaeto[27] demonstrated that leaf and root extracts of *Eichhornia crassipes* effectively inhibit mild steel corrosion in 5 mol L^{-1} HCl. The density functional theory (DFT)-based quantum chemical calculations revealed that parameters associated with the electronic and adsorption structures of phytochemical components present in the extracts explain the mechanism of the corrosion inhibition process.

Ashwe and Ikpambese[28] studied the potential of *Eichhornia crassipes* as a corrosion inhibitor using an artificial neural network. They were able to model a possible corrosion inhibition efficiency of 98 % for the leaf extract of *Eichhornia crassipes* tested on steel in H_2SO_4.

The use of water hyacinth extract as a corrosion inhibitor for other materials such as aluminum, magnesium, and cast iron has been investigated[21,23,29–31]. All investigations have shown a significant corrosion inhibition capacity of extracts obtained from water hyacinth. For aluminum in 0.5 mol L^{-1} NaOH solution, a decrease in corrosion rate of up to 98 % has been reported[21].

Investigating water hyacinth extracts as green corrosion inhibitors offers an opportunity to address the environmental challenges posed by this invasive species. By valorizing water hyacinth, we can control its spread and develop eco-friendly corrosion prevention solutions[15]. Despite several studies in the literature that explore the potential use of *Eichhornia crassipes* as corrosion inhibitor for steel, the comparison between the inhibition efficiency of different parts of the plant is usually not investigated. In addition, it is important to conduct research to compare the performance of the species collected in Brazil with the species that have been collected and tested as corrosion inhibitors in other parts of the world. Hence, the objective of this research was to explore the potential of *Eichhornia crassipes* extracts obtained from roots and leaves as corrosion inhibitors for sustainable corrosion protection. To achieve this, the study employed various techniques, including electrochemical and weight loss measurements, as well as recording microscope photographs. The results enabled the evaluation of the inhibition efficiency.

Experimental

Materials and samples preparation

Square-shaped samples of AISI 1005 steel (chemical composition determined by optical emission spectrometry: 0.042 C, 0.23 Mn, 0.023 Si, 0.0088 P, 0.0130 S and balance Fe (wt%)) with approximate dimensions of 2.25 cm x 2.25 cm x 1.00 mm were used in this work. The samples were mechanically ground using 80 to P1200 grit emery paper. For electrochemical tests, a copper wire electrical connection was brazed and the surface was masked with a 3M™ galvanic tape, leaving an exposed test area of 2.00 cm². Before every test, the samples were cleaned via sonication for 1 minute in deionized water, acetone, and then dried by air blowing.

Inhibitor extraction

Aqueous extracts were obtained from both the leaf and the root of water hyacinth. The *Eichhornia crassipes* (EC) samples (Fig. 1) were collected at Porto Geral in the city of Ladário/Brazil (19º00’02”S, 57º36’05”W) on September 12, 2022, for the preparation of root extracts, and on September 27, 2022, for leaf extracts. The electrolytes were prepared on the same day as their collection, and the experimental tests were conducted 48 hours after collection to minimize degradation of the organic material present in the solution.

After collection, the leaf and the root were separated from the rest of the plant and mashed independently by mortar and pestle. Then, 50.00 g (measured after mashing) of the macerated pulp was added to 1 L of 0.01 mol L^{-1} HCl (QHEMIS HCl 37 % PA ACS) aqueous solution, which was subjected to sonication for 2 hours at 23 ± 1 ºC [13]. The extract remained within the solution for an additional 22 hours, totaling 24 hours. At the end of this time, the solution was sieved to remove the solid pulp. The procedures were the same for both leaf and root extraction. The final concentrations obtained were 2.10 ± 0.03 g L^{-1} and 0.723 ± 0.12 g L^{-1} for leaf and root extracts, respectively, which were determined by the evaporation technique.

Fig. 1 – *Water hyacinth*

The concentration values differed because the raw mass of each part of *Eichhornia crassipes* was considered during the extraction process. This suggests that the extraction method used may have favored a higher solubility of the leaf extract components compared to those of the root extract.

Corrosion tests

The corrosion tests were carried out to evaluate the inhibition effect of the extracts produced in aqueous solution of 0.01 mol L^{-1} HCl (QHEMIS HCl 37 % PA ACS) with and without EC leaf and root extracts.

Electrochemical tests were performed in a conventional three-electrode working cell, consisting of a working electrode (WE) made of AISI 1005 steel, a reference electrode (RE) of saturated calomel (SCE), and a platinum wire as counter electrode (CE). The tests were performed using an AUTOLAB PGSTAT302N potentiostat/galvanostat. Open circuit potential (OCP) measurements were conducted for a period of 30 minutes (1800 seconds) in electrolytes with and without the presence of the extracts.

Potentiodynamic polarization curves were carried out to study the electrochemical behavior of steel in the presence and absence of an inhibitor. For the potentiodynamic polarization tests, the samples were left at OCP for 30 minutes. Subsequently, the polarization test started from the cathodic direction at –250 mV vs OCP to the anodic direction up to +250 mV vs OCP, with a scan rate of 1.0 mV s^{-1}. The data were recorded and analyzed using the NOVA 2.1.4 software.

Weight loss (WL) tests were conducted by immersing the samples into 250 mL of the corrosive solutions (0.01 mol L^{-1} HCl with and without the addition of the extracts) in open air at 23 ± 1 ºC for 120 hours (5 days), to determine the inhibition efficiency of leaf and root extracts obtained from *EC*[32,33]. The cleaning procedures were adapted from ASTM standard G1-03[33]: after the immersion time, the samples were cleaned with deionized water, dried by air blowing, and then subjected to sonication in acetone for 5 minutes to remove any corrosion products embedded on the metal surface. Additionally, a soft brush was used for abrasive removal of non-metallic materials from the sample surface. Once properly dried, the masses of the samples were measured to calculate the corrosion rate according to Equation (1).

$$CR = \frac{K \cdot W}{A \cdot t \cdot d} \tag{1}$$

where *CR* is the abbreviation for corrosion rate, constant $K = 8.76 \cdot 10^4$ mm year^{-1}, *W* is the weight loss in grams (g), *A* is the area in cm^2, *t* is the time in h, and *d* is the density of the material (7.874 g cm^{-3} for AISI 1005 steel)[13,33].

The inhibition efficiency (η/%) can be obtained from the WL data by Equation (2), where W_0 is the weight loss without inhibitor in solution, and *W* is the weight loss in the presence of inhibitor in solution[7,21].

$$\eta/\% = \left(1 - \frac{W}{W_0}\right) \cdot 100 \tag{2}$$

All corrosion tests were conducted in triplicate, and the results are shown as mean ± standard deviation values. Additionally, one-way analysis of variance (ANOVA) was performed with significance set at $p \leq 0.05$. Significant differences were then distinguished using Duncan's test.

Morphological analysis

Macroscopic and microscopic analyses of the steel surface were performed after the WL tests (after cleaning the samples) to evaluate the extent of the corrosion and its morphology in solutions with and without the addition of the corrosion inhibitors. Macroscopic images were obtained using a digital camera of a Xiaomi POCO X3 smartphone, and microscopic analyses were performed using a Edutec N.S.A012844 Microscope.

Results and discussion

OCP measurements

The results of the OCP over time in the different electrolytes are shown in Fig. 2. In the presence of leaf and root extracts, the electrode potential increased approximately +90 mV and +40 mV, respectively, within the first 5 minutes of testing. Notably, the initial potentials were lower than those observed in the blank test. This variation can be attributed to the presence of compounds in the extracts in the solution, such as aromatic compounds, nitrogen, phosphorus, which may have adsorbed onto the steel surface, causing a shift in the potential[32].

The potential in the blank solution (without the addition of extracts) showed a slight variation of approximately +20 mV in the first 2 minutes of testing, which can be attributed to the reactivity of the steel when immersed in the HCl electrolyte, which stabilized shortly after, with stable potential values for the remainder of the test[32].

The presence of the extracts caused slight shifts in the potential towards more negative values, which may indicate a thermodynamic tendency for the metal to undergo oxidation[7]. However, in some cases, organic inhibitors can exhibit an effect that favors corrosion inhibition by reducing the velocity

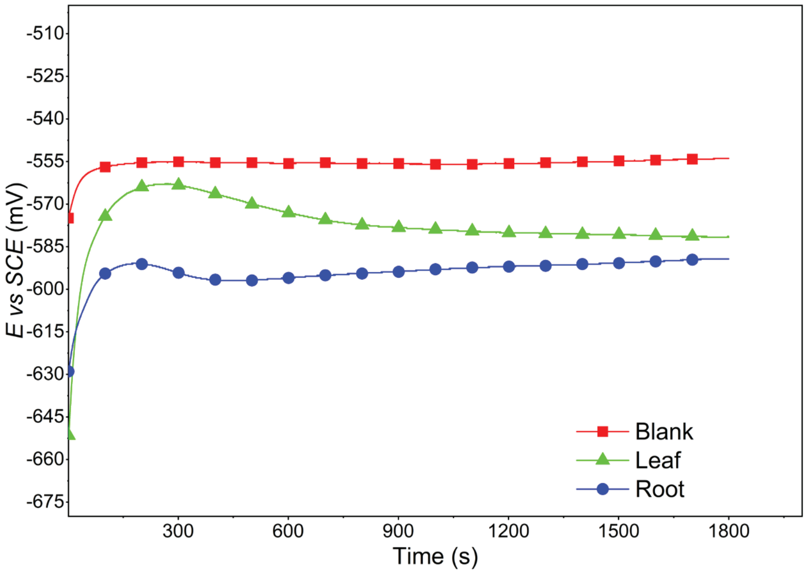


Fig. 2 – *Open circuit potential (OCP) of AISI 1005 steel in HCl 0.01 mol L^{-1} solution with and without addition of water hyacinth root and leaf extracts*

Table 1 – *Potentiodynamic polarization parameters for mild steel in the absence and presence of the studied extract as corrosion inhibitor*

Inhibitor	E_{corr} (V)	j_{corr} (A cm^{-2})	Corrosion rate (mm year^{-1})	η (%)	θ	$\lvert b_a \rvert$ (V dec^{-1})	$\lvert b_c \rvert$ (V dec^{-1})
0.01 mol L^{-1} HCl (Blank)	–0.566	$5.90\cdot10^{-5}$	0.686	–	–	0.151	0.241
Leaf extract	–0.578	$3.40\cdot10^{-5}$	0.395	42.4	0.42	0.107	0.445
Root extract	–0.585	$3.78\cdot10^{-5}$	0.440	35.9	0.36	0.122	0.332

of cathodic reactions without apparently modifying the velocity of anodic reactions, leading to a shift in the OCP towards more negative values, as observed in Fig. 2. Therefore, it would result in a reduction of cathodic current density, which consequently reduces the corrosion rate[7].

Potentiodynamic polarization measurements

The polarization curves, (Fig. 3), show that the E_{corr} values shift towards more negative potentials in the systems containing the extracts. According to the literature[23], a corrosion inhibitor may be classified as anodic or cathodic only if the difference between the E_{corr} values in the absence and presence of the inhibitor is greater than ±85 mV. Based on these criteria, the results indicated that both inhibitors produced in this work exhibited mixed-type inhibition behavior with a slight preference for cathodic inhibition. This is evident by the shift towards more negative values compared to the blank solution (approximately –12 mV and –19 mV for leaf and root extracts, respectively).

At any applied potential in the cathodic region, a decrease in current density was observed in tests conducted with the addition of extracts compared to those observed in the blank solution. This indicated that the reaction rate in the cathodic region was reduced in the presence of extracts, meaning that the cathodic reactions are being effectively hindered[34].

Table 1 presents the data extracted from the potentiodynamic polarizations tests, along with the ANOVA statistical analysis, allowing for several conclusions to be drawn. The addition of a corrosion inhibitor significantly affected the E_{corr} value (p=0.001326). The Duncan test showed that each group (blank, root, and leaf) differed significantly from each other in terms of E_{corr}, with the E_{corr} values ranking as Root < Leaf < Blank. Similarly, the addition of a corrosion inhibitor had a significant effect on the j_{corr} value (p=0.000368). The Duncan test revealed that the groups with inhibitors (root and leaf) differed significantly from the blank group, exhibiting a significantly lower j_{corr} value. However, no significant difference was observed between the types of inhibitors (root or leaf) in

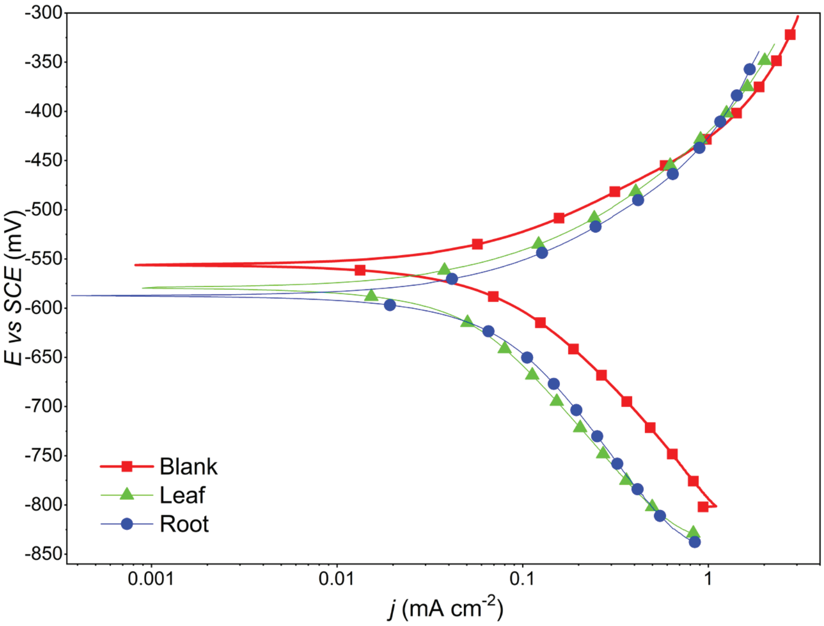


Fig. 3 – *Potentiodynamic polarization curves of AISI 1005 steel in HCl 0.01 mol L^{-1} solution with and without addition of water hyacinth root and leaf extracts*

terms of j_{corr}, as they do not differ statistically from each other.

On the other hand, the addition of a corrosion inhibitor did not significantly affect the b_a value (p=0.082354). Conversely, the addition of a corrosion inhibitor significantly affected the b_c value (p=0.002797). The Duncan test indicated that each group (blank, root, and leaf) differed significantly from each other in terms of the b_c value, with the b_c values ranking as Leaf > Root > Blank. This indicated that the inhibitors possessed a cathodic character.

Table 1 also reveals that the corrosion inhibition efficiency was 42.4 % for the leaf extract and 35.9 % for the root extract. This difference can be explained by the higher amount of inhibitory compounds present in the leaf[27]. The degree of surface coverage, θ, obtained from the polarization curves ($\theta = \eta(\%)/100$) was also calculated.

An interesting effect emerged when comparing the E_{corr} and b_c values between the leaf and the root extracts. The E_{corr} for the root was lower than that for the leaf, while the b_c value for the leaf was greater than that for the root. This suggests that the physical blocking effect (physical adsorption) in the cathodic reaction played a more significant role than any changes in the cathodic reaction mechanism (b_c). Theoretically, physical adsorption does not alter b_c (nor b_a). However, if a larger amount of inhibitor adsorbs during the cathodic reaction, the entire cathodic curve would shift to the left, resulting in a lower E_{corr}.

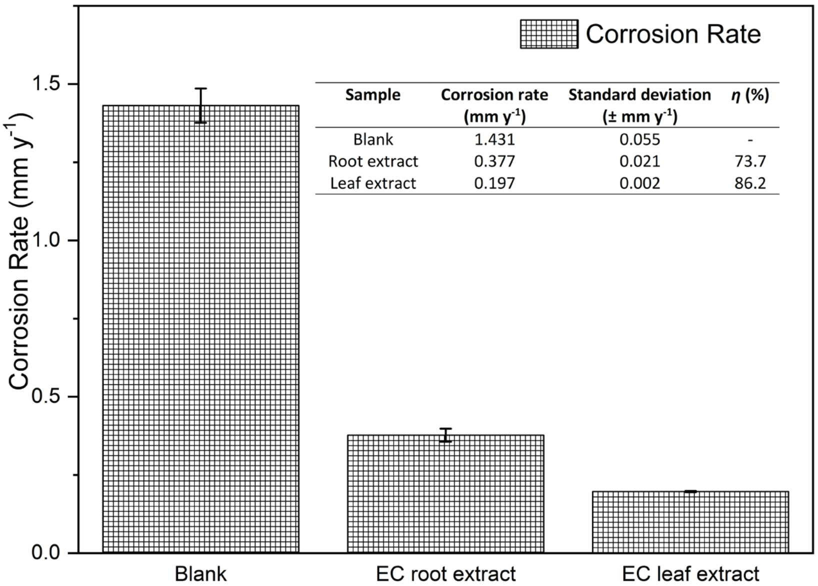
These significant changes in E_{corr}, j_{corr}, and b_c (as confirmed by ANOVA analyses) suggest that this inhibitor exhibited a mixed mode of action. It provided surface blocking (via physical adsorption) during the cathodic reaction, shifting the entire cathodic polarization curve to the left, and also altered the mechanism of the cathodic reaction (as evidenced by changes in b_c), thereby increasing the polarization of this reaction.

As previously mentioned, the shift of E_{corr} towards more negative values and the reduction in cathodic current density indicate a relationship with the OCP curves, as there was a decrease in the rate of cathodic reactions, favoring corrosion inhibition[7].

Weight loss measurements

Weight loss (WL) measurements provide a means to determine both the corrosion rate (CR) and the inhibition efficiency ($\eta(\%)$) after an immersion test conducted without applied potential[19,20]. These data are presented in Fig. 4. In the blank solution (without extract), the CR reached approximately 1.4 mm year^{-1}. When the root extract was added to the solution, the CR was 0.4 mm year^{-1}. Similarly, with the addition of leaf extract, the CR dropped to approximately 0.2 mm year^{-1}. These findings indicate reductions in CR of approximately 3.5 and 7 times for the systems containing root and leaf extracts, respectively.

The extracts demonstrated an inhibition efficiency value of 86.2 % for the leaf extract, and 73.7 % for the root extract. These results indicate their potential as green inhibitors for steel corrosion in media containing hydrochloric acid as the aggressive agent. Electrochemical polarization yielded in-



Sample	Corrosion rate (mm y^{-1})	Standard deviation (± mm y^{-1})	*η* (%)
Blank	1.431	0.055	-
Root extract	0.377	0.021	73.7
Leaf extract	0.197	0.002	86.2

Fig. 4 – *Corrosion rate of mild steel in 0.01 mol L^{-1} HCl with and without EC leaf and root extract*

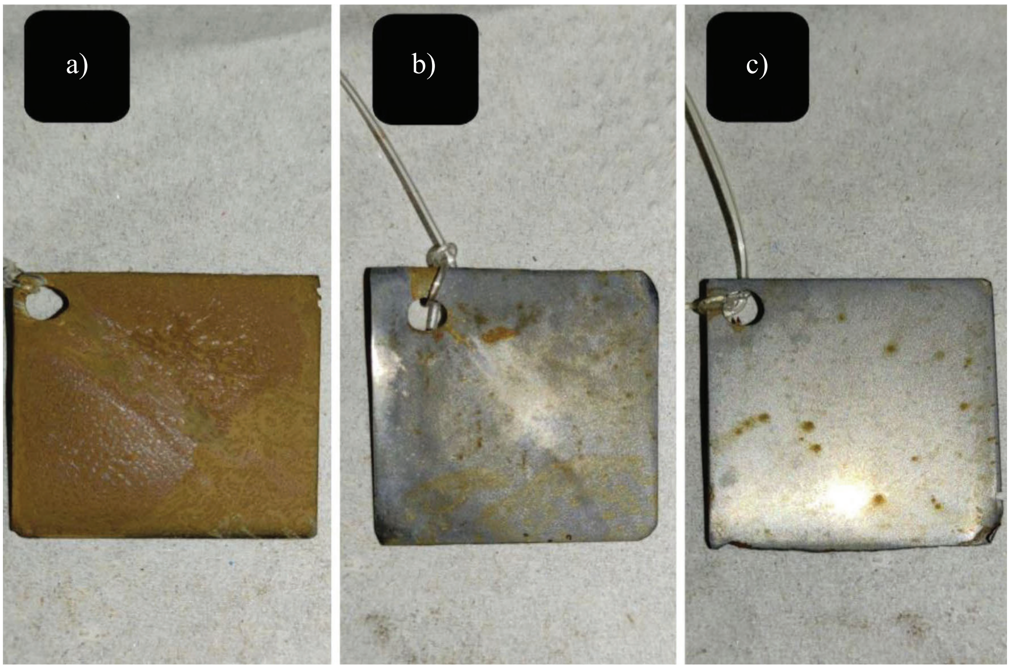


Fig. 5 – *Macroscopic view of the samples after weight loss tests: (a) blank system, (b) root system, and (c) leaf system*

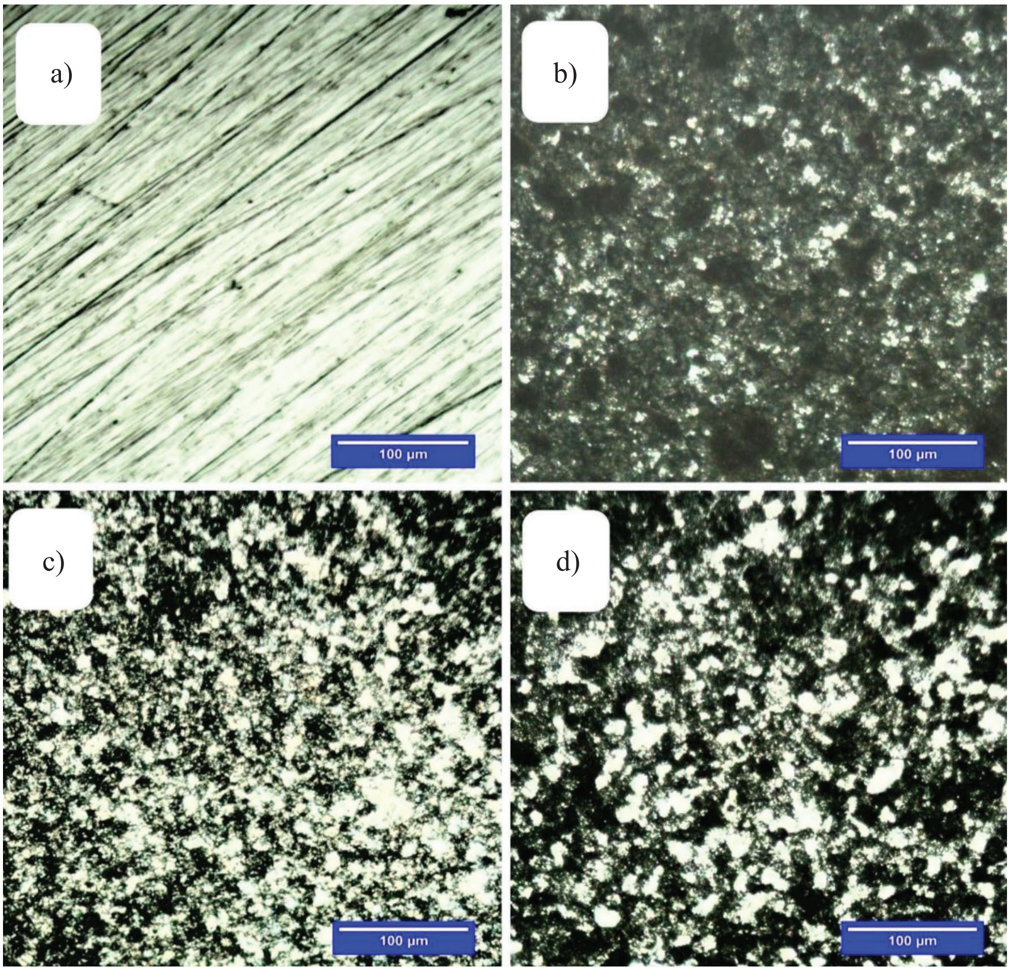


Fig. 6 – *Images obtained via optical microscopy: (a) steel before testing, (b) blank system, (c) leaf system, and (d) root system*

hibition efficiencies of 42.4 % and 35.9 % for leaf and root extracts, respectively, showing a minimal difference of only 6 %. The inhibition efficiencies obtained from weight loss experiments were approximately twice those observed through polarization. These differences in inhibition efficiencies between polarization and weight loss can be as attributed to several factors: a) Different active species – Under polarization conditions, different active species may be involved in the inhibition mechanism compared to those in weight loss experiments. This could be due to the applied potential influencing the adsorption and interaction of the extract molecules with the metal surface; b) Electrochemical conditions – The electrochemical conditions differ between the experiments. Polarization involves an applied potential, while weight loss occurs under open-circuit conditions. These different conditions can affect the effectiveness of the extract molecules in inhibiting corrosion; c) Mass transfer limitations – In weight loss experiments, mass transfer limitations may play a role in the observed inhibition efficiency. The diffusion rate of the extract molecules to the metal surface could influence their ability to protect the metal from corrosion; d) Synergy and interactions – The longer exposure during weight loss experiments may allow for the development of synergies and interactions between the extract molecules, the corrosive medium, corrosion products, and the metal surface. These interactions could enhance the inhibition efficiency observed in the weight loss experiments compared to polarization.

Moreover, it is important to emphasize that the levels of crude protein, nitrogen, soluble carbohydrates, polyphenols, and phosphorus present in the plant structure, which are considered essential for an effective green corrosion inhibitor, might have been a key point for the promising results obtained in the tests, demonstrating their importance in the composition of an inhibitor[1,17].

Despite the complex nature of *E. crassipes* extract, its overall corrosion inhibition effect likely stems from the combined action of various components. The alkaloids, steroids, carboxylic acids, and phthalate derivatives present in the EC extracts have functional groups (double bonds, carbonyl, hydroxyl, and amines) with inhibitory properties that can form protective layers on the metal surface[17–21,35]. DFT calculations[27] further support this by revealing potential interactions of individual constituents with the metal surface, contributing to the overall barrier effect observed in our experiments.

Morphological analysis

Fig. 5 presents the macroscopic view of the samples after the weight loss immersion tests. Notably, there is a clear difference between the blank system, which exhibits a generalized corrosive process, and the systems treated with inhibitors, where corrosion marks are visible, but with preserved characteristics of the base metal (steel).

Fig. 6 presents micrographic images of the specimen surfaces both before and after WL tests, in solutions with and without the addition of extracts. Fig. 6(a) depicts the microscopic view of the surface prior to testing, revealing a typical as-ground condition. Figs. 6(b-d) illustrate the surface after the WL tests. The darker regions in these images indicate the formation of corrosion products on the surface, while the brighter areas correspond to the steel itself.

The surface of the blank system, shown in Fig. 6(b), exhibits characteristics of generalized corrosion. In Fig. 6(c), the surface of the specimen with leaf extract displays some corrosion products, but the base metal is significantly more visible compared to the blank system. Fig. 6(d) shows the specimen after testing in the system containing the root extract, where the corrosion products and the base metal are more balanced, with fewer corrosion marks than in the blank system.

In conclusion, the system without extract demonstrated greater corrosion marks, while the presence of extracts contributed to a less attacked surface.

Conclusions

The effect of adding *EC* leaf and root extracts to 0.01 mol L^{-1} HCl solutions on the corrosion of AISI 1005 steel was investigated, leading to the following conclusions:

1) Weight loss measurements indicated satisfactory inhibition efficiency, with the leaf extract achieving 86.2 % and the root extract 73.7 %;
2) The extracts exhibited mixed-type inhibition behavior, with a slight preference for cathodic processes;
3) The extracts reduced the formation of corrosion products on the steel surface, with the leaf extract showing a greater ability to preserve the base metal, leaving it significantly less corroded.

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