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Marine Octocoral *Phyllogorgia dilatata*: Identification of Sesquiterpenes and Activity as a Natural and Renewable Corrosion Inhibitor

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Abstract- In the context of highly efficient, non-toxic and natural organic corrosion inhibitors, *Phyllogorgia dilatata* was studied as an anticorrosive for mild steel in acid medium. The marine octocoral crude extract (PDCE) was characterized and analyzed by LC-HRMS, revealing the presence of 16 different organic molecules. The corrosion inhibition was evaluated via weight loss study and electrochemical techniques. The obtained polarization curves showed that PDCE acts as a mixed-type inhibitor and gravimetric, Electrochemical Impedance Spectroscopy and Linear Polarization Resistance analyses reached an average maximum anticorrosive efficiency of 93.4% at 1 g L⁻¹. The data crossing between gravimetric and electrochemical measurements indicated that the protection mechanism is due to adsorption, blocking electro-active sites. The adsorption data followed the Freundlich theory and SEM/EDX images confirmed the formation of a protective multilayer film.

Keywords- *Phyllogorgia dilatata*; Natural corrosion inhibitor; Mild steel; Acidic medium Electrochemical measurements; Surface characterization

1. INTRODUCTION

Metallic corrosion is a serious problem that generates billion-dollar economic losses to many countries around the globe. It can also cause irreparable damage to human life and to the environmental system [1-6].

Acid medium is one of many harmful and aggressive mediums that can cause the severe problems cited above. Hydrochloric acid (HCl) is a very common electrolyte solution used by a wide range of industries with a variety of functions, such as pickling, cleaning and descaling. Mild steel (MD) is one of the most used metal alloys in the industrial field due to its low price and good mechanical properties. However, due to the lack of alloy elements (such as chromium, molybdenum, vanadium and nickel), MD is highly susceptible to corrosive process, especially in 1 mol L⁻¹ HCl solutions [7,8].

Organic corrosion inhibitors are a great alternative to minimize corrosion. Due to structural elements (heteroatoms with non-bond electrons pair and π -electrons), these molecules can interact with elements from the alloy and adsorb on metal surface, forming a protective film, preventing the contact with the aggressive medium. They directly solve the corrosion problem, but there are some problems related to the use of these compounds: expensive and waste-generating synthetic routes and noxious products, being environmentally dangerous and not viable [9-13].

An excellent alternative is the use of inhibitors from natural sources. Several studies in the literature have shown the usage of extracts from plants and fruits as great corrosion inhibitors in different corrosive mediums [14-24]. The vast biodiversity of the marine environment has already proved to be a valuable alternative in the investigation for active compounds with singular chemical structures capable of being eco-friendly inhibitors, especially with algae extracts [25-30]. Recently, our research group pioneered the study of a marine sponge as corrosion inhibitor for mild steel in acid medium and *Ircinia strobilina* crude extract showed 82% efficiency at 2.0 g L⁻¹ [31]. In addition, methods have been developed to allow the cultivation of these organisms or their cells in artificial or natural environments making viable their use as biomaterial [32,33].

The Brazilian marine invertebrate *Phyllogorgia dilatata* Esper (Gorgoniidae family), also known as elephant ear, it's a octocoral specie that can be found in sub-tidal environments with frequent and shallow water reefs distributed along the southwest Atlantic from Maranhão State to Rio de Janeiro, Brazil [34]. It has already been reported antimicrobial [34], antifouling and feeding deterrent activity for this species [35,36]. Additionally, sesquiterpenic compounds with interesting odoriferous potential for use in perfumery can be obtained [37].

In this work, the authors reported for the first time the usage of a marine octocoral crude extract as corrosion inhibitor for mild steel in acid medium. *Phyllogorgia dilatata* crude extract was studied by gravimetric and electrochemical (Electrochemical Impedance Spectroscopy, Linear Polarization Resistance and Potentiodynamic Polarization) methods and

the mild steel surface was analyzed by Scanning Electron Microscopy. All the results show that *P. dilatata* is a great newly natural and renewable corrosion inhibitor, forming a protective film that prevents the contact with the aggressive medium.

2. EXPERIMENTAL

2.1. Material and methods

2.1.1. Collection and identification of octocoral material

The *Phyllogorgia dilatata* specimen was collected in December 1995, at Armação dos Búzios, Rio de Janeiro State, Brazil (22°45′S; 41°51′W), to a depth between 3 and 5 m. Taxonomic identification was performed as described in previous works [38,35]. A voucher specimen (PD1295) has been deposited at *Instituto de Química-UFF*.

2.2. Preparation of crude extract

The biological material was air dried for 2 hours and kept frozen until extraction. *Phyllogorgia dilatata* (1,364 g of dry weight) was then cut into small pieces and extracted by static maceration once with a mixture of methanol/dichloromethane, 1:1 (during 6 hours), and twice with pure dichloromethane (during 20 hours each). The extracts were combined and evaporated under reduced pressure yielding 151 g of a viscous dark brown crude extract (11% of dry weight).

2.3. Chemical characterization by Liquid chromatography-high resolution mass spectrometry analysis (LC-HRMS)

The LC-HRMS/MS analysis of *Phyllogorgia dilatata* crude extract (PDCE - 3 mg mL⁻¹) was performed on an ultra-high-performance liquid chromatography (UHPLC) system (model Nexera®, Shimadzu) consisted of two quaternary LC-30AD pumps, DGU-20A5R degasser, SIL-20AC autoinjector, SPD-30MA diode array detector, CTO-20AC column oven, a six-column selector valve, and a CBM-20A interface, coupled to a high-resolution mass spectrometer (HRMS) containing a quadrupole time-of-flight mass analyzer (QTOF) (Impact HD, Bruker Daltonics) equipped with an electrospray ionization (ESI) source (FAPESP 2014/50244-6). The chromatographic conditions used were: Acquity UPLC BEH C18 (Waters®, 50×2.1 mm, 1.7 μ m) column in a linear gradient elution at 0.4 mL min⁻¹ and temperature set at 30 °C, with solvent A (0.1% formic acid in ultrapure water v/v) and B (acetonitrile) varying from 30 to 80% of B in 20 min and kept at this concentration for 1 min; then the initial condition was reestablished (30% B) and kept for 4 min at this concentration (total run time of 25 min); the injection volume was 5.0 μ L. The ESI source conditions were: 4500 V for the capillary voltage, 500 V for the end plate offset, 1.0 bar for the nebulizer

pressure (N₂), 8.0 L min⁻¹ and 200 °C for the dry gas flow rate and temperature (N₂) and 8 eV for collision cell energy. All the analyses were carried out in positive ion mode, for a range of m/z 100-1000. The mass spectrometer was programmed to perform acquisition in auto MS/MS mode (number of precursors 4) in experiments with different collision energy between 18 and 45 eV for all m/z range analyzed.

The acquired data were converted to mzXML format and submitted to Global Natural Products Social Molecular Network (GNPS; http://gnps.ucsd.edu) online system for molecular network (MN) calculations and database matching. MN were constructed using 0.02 Da as precursor ion mass tolerance and 0.02 Da as fragment ion mass tolerance, 0.7 as minimum cosine score and 4 as minimum matched fragment ions for edge linkage.

2.4. Gravimetric studies and electrochemical measurements

The gravimetric studies were performed according to the rules of the American Society for Testing Materials (ASTM G1 - 03) and the electrochemical measurements were carried out using an Autolab 128N potenciostat/galvanostat with a three-electrode cell (WE–mild steel, RE–Ag|AgCl, CE–Pt). After measuring the Open Circuit Potential (OCP) for 3600 s, Electrochemical Impedance Spectroscopy was carried out in the range of 100 kHz-10 mHz at the OCP with an amplitude of 10 mV. Linear Polarization Resistance was executed at \pm 10 mV *vs.* OCP and Potentiodynamic Polarization was performed at \pm 300 mV *vs.* OCP. All data were analyzed with NOVA Software. Fernandes et al. previously described the methodology used [39].

2.5.Surface analysis

Scanning Electron Microscopy was performed on a Quanta 250 FEG (ThermoFishcer Scientific) under vacuum.

3. RESULTS AND DISCUSSION

3.1. Phyllogorgia dilatata crude extract (PDCE) characterization

The chemical characterization of PDCE was performed by identifying compounds based on high resolution mass data acquired by LC-HRMS/MS analysis. The results were submitted to the GNPS database that allowed to infer seven compounds (1-7). In addition, nine other compounds (8-16) (Table 1) already reported in *P. dilatata* [37,40] were also identified in the PDCE extract by mass data analysis. The molecular structures are shown in Fig. 1.

All the compounds identified in the octocoral contain heteroatoms and multiple bonds that are structure elements known to exhibit corrosion inhibiting properties toward metals [41].

Compounds	Molecular Formula	Exact Mass (Da)	Error (ppm)	Ion
Curcumenol (1)	$C_{15}H_{22}O_2$	234.1620	0	$[M+H]^+$
Farnesol (2)	C ₁₅ H ₂₆ O	222.1984	4	$[M+H]^+$
15(S)-Hydroxy-(5Z,8Z,11Z,13E)-eicosatetraenoic acid (3)	$C_{20}H_{32}O_{3}$	320.2351	3	$[M+H]^+$
Pinolenic acid (4)	$C_{18}H_{30}O_2$	278.2246	7	$[M+H]^+$
(22 <i>E</i>)-5α,8α-Epidioxyergosta-6,22-dien-3β-ol (5)	$C_{28}H_{44}O_3$	428.3290	4	$[M\text{+}H\text{-}H_2O]^+$
Curcumol (6)	$C_{15}H_{24}O_2$	236.1776	2	$[M+H-H_2O]^+$
Linoleyl alcohol (7)	C ₁₈ H ₃₄ O	266.2610	4	$[M+H]^+$
<i>E,E-</i> Germacrone (8)	C ₁₅ H ₂₂ O	219.1749	3	$[M+H]^+$
<i>Z,E-</i> Germacrone (9)	C ₁₅ H ₂₂ O	219.1749	4	$[M+H]^+$
12-hydroxynardosin-1(10),11(13)-diene (10)	C ₁₅ H ₂₄ O	220.1827	3	$[M+H]^+$
11,12-epoxynardosin-l(l0)-ene (11)	C ₁₅ H ₂₄ O	220.1827	2	$[M+H]^+$
11β,12β-epoxypukalide (12)	$C_{20}H_{22}O_7$	374.1366	1	$[M+H]^+$
(<i>E</i>)-germacra-1(10),4(15),7(11)-trien-5-ol-8-one (13)	$C_{15}H_{22}O_2$	234.1620	2	$[M+H]^+$
4,5-epoxygermacra-1(10),7(11)-dien-8-one (14)	$C_{15}H_{22}O_2$	234.1620	2	$[M+H]^+$
Linoleic acid (15)	$C_{18}H_{32}O_2$	280.2402	1	$[M+H]^+$
Peridinin (16)	C ₃₉ H ₅₀ O ₇	630.3557	-1	$[M+H]^+$

Table 1. Substances identified in PDCE



Fig. 1. Molecular structures of inferred compounds in PDCE

3.2. Gravimetric studies

The first method to evaluate PDCE as a corrosion inhibitor for mild steel in acid medium was the gravimetric studies.



Fig. 2. PDCE concentration dependence on corrosion rate and anticorrosive efficiency

Fig. 2 shows that there is a drop in the corrosion rate (CR) with an increase in corrosion inhibitor concentration, consequently increasing the inhibition efficiency (η) [42,43]. As shown in Table 1, the various molecules that constitute PDCE have in their molecular structure π and n-electros, and it is well reported in literature that organic molecules with those characteristics act adsorbing on the metal surface to form a protective film against the aggressive medium [39,44-46]. Therefore, we can assume that the efficiency is associated with a surface coverage (θ) of the mild steel by PDCE.

Table 2 reports all the data. A greater value of θ can be attributed to the higher number of organic molecules adsorbed on the mild steel surface as the PDCE concentration in the electrolyte increases, pointing to the formation of a better protective film. The inhibitor reaches 91.6 % of anticorrosive efficiency at 1.0 g L⁻¹. Since is the first time that a marine octocoral extract is used as corrosion inhibitor, we were unable to compare the results with the literature. Despite that, comparing with other marine fauna already used, our CI has a great efficiency with a reasonable concentration [31,27,25,47].

Table 2.	Gravimetric	studies	data
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Concentration (g·L ⁻¹)	Corrosion Rate (mm per year)	η (%)	θ
Blank	1.935	0.0	0.000
0.1	0.724	62.6	0.626
0.3	0.527	72.8	0.728
0.5	0.373	80.3	0.803
0.8	0.258	86.7	0.867
1.0	0.162	91.6	0.916

3.3. Adsorption isotherm

The adsorption isotherm helps understand the interface inhibitor/film and the formation of the protective film depending on what theory the data best fit. With this purpose, ten different isotherms were simulated using the gravimetric studies results: Freundlich, Flory-Huggins, Temkin, Kiselev, Hill-de Boer, Frunkim, Langmuir, Dubinin-Radushkevic, Fowler-Guggenheim and Elovich [48,49].

PDCE data best fitted the Freundlich isotherm, one that define the adsorption as nonideal and reversible, not limited by a monolayer. It can ben mathematically expressed (Eq. 1) associating the surface coverage (θ), the inhibitor concentration (C_{inh}) and the adsorption equilibrium constant (K_{ads}) [48,50].

$$\log\theta = \log K_{ads} + \frac{1}{n} \log C_{inh}$$
(1)

Fig. 3 show the Freundlich plots for PDCE at different temperatures and their respective linear correlation coefficient that indicated a great fit ($R^2 > 0.99$ at all temperatures), suggesting that PDCE can form a multilayer protective film on the mild steel surface [51-53].

Table 3 shows the calculated adsorption constants (K_{ads}) and 1/n values. It can be seen that the raise of temperature favors PDCE adsorption on the mild steel surface, since the greater K_{ads} value, the more favorable is the adsorption. It is well reported in the literature that 1/n values between 0 and 1 are a characteristic of chemisorption process, agreeing with a higher adsorption constant at higher temperatures. It is also well reported that these values describe a more heterogeneous surface as they get closer to 0. This is in agreement with the system studied, since it is a carbon steel alloy, composed of several elements, and a crude extract as corrosion inhibitor, composed of 16 different molecules [54-58].



Fig. 3. Freundlich adsorption isotherm for PDCE on mild steel in acid medium at different temperatures

Temperature (K)	R ²	K _{ads} (g L ⁻¹)	1/n
298	0.9904	0.9042	0.1646
313	0.9901	0.9300	0.1476
328	0.9911	0.9634	0.1360

 Table 3. Freundlich isotherm data

The adsorption thermodynamic parameters, such as Gibbs free energy and variation of enthalpy and entropy, were not possible to be discussed, as reported by other authors, because crude extracts are formed by a large number of molecules, which makes their molecular mass unknown [31,59-61].

3.4. Kinetic corrosion parameters

To understand better the adsorption of organic molecules on the mild steel surface and the corrosion prevention process, some physical-chemical parameters were discussed. In order to do that, the experimental temperature was twice increased and gravimetric studies were again performed. The results are shown in Table 4.

	298 K		313 K		328 K	
Concentration (mmol·L ⁻¹)	Corrosion Rate (mm per year)	η (%)	Corrosion Rate (mm per year)	η (%)	Corrosion Rate (mm per year)	η (%)
Blank	1.935	0.0	12.083	0.0	38.057	0.0
0.1	0.724	62.6	4.030	66.6	11.446	69.9
0.3	0.527	72.8	2.759	77.2	6.407	83.2
0.5	0.373	80.3	2.007	83.4	4.559	88.0
0.8	0.258	86.7	1.314	89.1	2.654	93.0
1.0	0.162	91.6	0.648	94.6	1.467	96.1

Table 4. Corrosion rate PDCE concentrations dependence at different temperatures

It can be seen from the results in Table 4 that for all PDCE concentrations, the rise in temperature increased the corrosion inhibition. This fact can be associated with a chemical process of adsorption, where there are donation of electrons from the organic molecule to the vacant d orbital from iron and the bonds are favored by elevating temperature [31,62,63].

Then, corrosion kinetic parameters such as activation energy (E_a), variation of activation enthalpy (ΔH^*) and variation of activation entropy (ΔS^*) were calculated using the Arrhenius (Eq. 2) and Transition State Theory (Eq. 3) equations [64,65], respectively.

$$\ln CR = \ln A - \frac{E_a}{RT}$$
(2)

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right)$$
(3)

where A is the pre-exponential factor, R is the universal gas constant, T is the experimental temperature, N is Avogadro's number, and h is Planck's constant.

 E_a is obtained via slope and A is obtained via intercept from the plot shown in Fig. 4a. Analogously, ΔH^* is obtained via slope and ΔS^* is obtained via intercept from the plot shown in Fig. 4b. All data is listed in Table 5.



Fig. 4. Arrhenius (a) and Transition State Theory (b) plots for mild steel PDCE corrosion inhibition in acid medium

Concentration	Ea	Α	$\Delta \mathbf{H}^{*}$	$\Delta \mathbf{S}^{*}$
(g L ⁻¹)	(kJ mol ⁻¹)	(mm per year)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)
Blank	61.9	2.16×10 ¹¹	59.9	-34.7
1.0	30.0	7.07×10^{4}	43.9	-110.1

Table 5. PDCE corrosion inhibition kinetic parameters for mild steel in acid medium

The presence of 1.0 g L⁻¹ of PDCE lowers significantly the value of activation energy from the corrosion process (61.9 to 30.0 kJ mol⁻¹). If we assume that the inhibition is due to adsorption on the metal surface, the lower number of electroactive sites available for corrosion can explain the lower E_a . This fact is corroborated by the Arrhenius pre-exponential factor, which is associated with number of active sites in heterogeneous reactions. Thus, a lower value of A (7.07×10^4 compared to 2.16×10^{11}) supports the above theory [64,65]. A positive value of activation enthalpy points to an endothermic process, explaining why higher temperatures have higher corrosion rates. A negative value of activation entropy indicates a more orderly system in the presence of PDCE, decreasing the disorder in metal dissolution [66,67].

3.5. Electrochemical Impedance Spectroscopy (EIS)

Before every electrochemical experiment was performed, the Open Circuit Potential (OCP) was measured for 3600 s. Fig. 5 shows the OCP *vs* time plots for the blank and inhibited solutions. It is possible to observe that the presence of different concentrations of PDCE in the electrolyte caused a stability in potential values, unlike the blank solution, where the potential decreases with time, probably due to corrosion [31].



The Nyquist plots (Fig. 6) showed depressed semi-circles, due to surface inhomogeneity, that increased in diameter as the concentration of PDCE in the acid medium increased [68-70]. These curves, known as the capacitive loop, are related to charge transfer resistance (R_{ct}) and the bigger they are, the better the mild steel surface is protected [71-74].



Fig. 6. PDCE concentration dependence on Nyquist plots for mild steel corrosion in acid medium

Fig. 7 shows the Bode phase (7a) and Bode modulus (7b) plots. In the first, it is possible to observe only one peak that increases in height as the inhibitor concentration increases, pointing to a better capacitive response as more organic molecules are adsorbed on the metal surface [75]. In the second, it is clearly that the shape of the curves does not change as PDCE concentration increases, enhancing the absolute value of impedance in low frequency regions. This fact suggest that the adsorption of inhibitor does not drastically change the corrosion process mechanism [21,76].



Fig. 7. PDCE concentration influence in Bode phase (a) and Bode modulus (b) plots for mild steel in acid medium

The EIS data was fitted using an equivalent electrical circuit widely reported in literature [77-83]. It is composed of a solution resistance (R_s) in series with a charger transfer resistance (R_{ct}) in parallel with a constant phase element (CPE). CPE is used instead of a capacitance due to metal surface inhomogeneity. The choice for this circuit (Fig. 8) is based in low values (around 10⁻³) of χ^2 , which indicates a good fit [77]. All data obtained via equivalent circuit is listed in Table 6.



Fig. 8. Electrochemical equivalent circuit used to fit EIS data

The double layer capacitance (C_{dl}) values were calculated using Brug's formula (Eq. 4) [39], since the corrosion rate in the non-ideally polarize electrode is controlled by slow charger transfer.

$$C_{dl} = Y_0^{1/n} \cdot \left(\frac{1}{R_s} + \frac{1}{R_{ct}}\right)^{(n-1)/n}$$
(4)

The numeric values listed in Table 6 can be associated with the Helmholtz model (Eq. 5) [39], that define C_{dl} being the product of air permittivity (ϵ^0), local dielectric constant (ϵ) and electrode surface (S) divided by film thickness (d).

$$C_{dl} = \frac{\varepsilon^o \varepsilon S}{d} \tag{5}$$

Table 6. EIS parameters for mild steel in acid medium without and with various concentrations of PDCE

Conc.	Rs	CP	E	C _{dl}	R _{ct}	ղ
(g L ⁻¹)	$(\Omega \ \mathrm{cm}^2)$	$Y_0 (μΩ^{-1})$ S ⁿ cm ⁻²	n	(μF cm ⁻²)	$(\Omega \ \mathrm{cm}^2)$	(%)
Blank	2.58	70.0	0.958	47.8	39.1	-
0.1	2.63	90.0	0.811	15.1	124.8	68.7
0.3	2.72	85.2	0.793	9.5	146.2	73.3
0.5	2.27	74.0	0.800	8.4	164.8	76.3
0.8	2.46	57.1	0.817	7.8	234.8	83.5
1.0	2.60	46.3	0.822	6.6	588.1	93.4

The lower values of double layer capacitance in the presence of PDCE compared to the blank solution can be explained by the diminishing of local dielectric constant and exposed electrode surface with the substitution of water molecules on the mild steel surface by adsorbed organic molecules. Besides that, the increase in film thickness value with more inhibitor molecules adsorbed also contribute to lower values of C_{dl} [84-87].

To better understand the diminishing values of C_{dl} as the inhibitor concentration increases, a plot of double-layer capacitance versus the relative electroactive area (1– θ , obtained via Gravimetric Studies) was made. Previously works published by our research group show that the formation of a protective monolayer implies a linear change in C_{dl} values relative to the relative electroactive area [39,31].



Fig. 9. Cdl versus relative electroactive area plot

Fig. 9 shows a non-linear correlation between C_{dl} and S (or 1– θ), which implies that the ratio ϵ/d is not constant, since ϵ^0 is always constant. This fact points to a significant change in film thickness (d) and local dielectric constant (ϵ) due to the multilayer adsorption of PDCE adsorbed on the mild steel surface, being in accordance to the Freundlich theory, [39,31] showed at section 3.3.

The increase in R_{ct} values as the PDCE concentration increases points to a better protection of the surface due to more organic molecules adsorbed on the metal, forming a protective film that prevent the contact with the aggressive medium, hindering the corrosion process. A maximum efficiency of 93.4% is obtained at 1.0 g.L⁻¹, being in agreement with gravimetric data [39,88,89].

3.6. Linear Polarization Resistance (LPR)

The other electrochemical study performed to evaluate the corrosion inhibition efficiency of PDCE was LPR. The polarization resistance (R_p) was obtained from the inverse of the slope in the current density *vs* potential plots (Eq. 6) [31].

$$\frac{dj}{dE} = \frac{1}{R_{\rm p}} \tag{6}$$

From the data shown in Table 7 is possible to observe that R_p increases in a nonlinear form as the PDCE concentration increases, suggesting less electroactive sites available for corrosion due to adsorption of organic molecules on the metal surface [90].

Table 7. LPR data for mild steel in acid medium without and with various concentrations of PDCE

Concentration	$\mathbf{R}_{\mathbf{p}}$	η
(g L ⁻¹)	$(\Omega \text{ cm}^2)$	(%)
Blank	48.2	-
0.1	142.6	64.2
0.3	166.2	71.0
0.5	191.6	74.8
0.8	272.5	82.3
1.0	669.4	92.8

Fernandes et al. [39,31] reported for corrosion process, that for the formation of a protective monolayer, a linear trend can be found when the inhibitor concentration is plotted *versus* the polarization resistance normalized by the relative electroactive area (1- θ), i.e. surface not coverage by organic molecules. Fig. 10 shows that the data crossing between

gravimetric and electrochemical measurements for a protective multilayer also showed a linear trend that intercepts the Y-axis (absence of inhibitor) at 44.8 Ω cm², very close to the experimentally obtained blank R_p (48.2 Ω cm²). This fact shows that the polarization resistance values when normalized by the relative electroactive area refer only to the area exposed to the corrosive medium and are not affected by the formation of mono or multilayer. Hence, PDCE is acting mainly adsorbing on the mild steel surface, diminishing the active sites, preventing the corrosive process [31,39].



Fig. 10. Plot of normalized polarization resistance versus inhibitor concentration

3.7. Potentiodynamic Polarization (PP)

Potentiodynamic Polarization was the last electrochemical measurement performed. Fig. 11 shows the polarization curves and a decrease in values of anodic and cathodic current is evident in the presence of PDCE, pointing to the inhibition of metal dissolution and hydrogen evolution by adsorption on mild steel surface [91].



Fig. 11. Polarization curves for mild steel in acid medium without and with various concentrations of PDCE

A more pronounced decay is observed as the inhibitor concentration increases [92,78,93,94].

Table 8 displays the values of corrosion potential (E_{corr}). A shift in this potential in the range of +4 mV to +33 mV is observed in the presence of PDCE in relation to the blank solution. It is well known in literature that mixed-type inhibitors change E_{corr} in a range of ±85 mV compared to the blank solution, thus characterizing PDCE in this category [11,95,96,78].

Table 8. PDCE concentration dependence on PP data for mild steel corrosion in acid medium

Concentration (g.L ⁻¹)	E _{corr} (V)
Blank	-0.470
0.1	-0.453
0.3	-0.439
0.5	-0.437
0.8	-0.464
1.0	-0.466





Fig. 12. SEM images of mild steel after (a) polishing and (b) 5 hours immersed in acid medium and the corresponding EDS data (a' and b')

3.8. Scanning Electron Microscopy (SEM)

Mild steel surface was analyzed by SEM with EDS at three different scenarios: after polishing, after 5 hours immersed in acid medium without inhibitor and after 5 hours

a')

9 10

immersed in acid medium with 1.0 g L^{-1} of PDCE, as shown in Fig. 12 and Fig. 13 [97-99]. The metal surface in the absence of inhibitor is much corroded due to hydrochloric acid attack (Fig. 12b), with EDS (Fig. 12b') pointing to the formation of iron oxide (corrosion product) [100-102].

With 1.0 g L⁻¹ of PDCE in the aggressive medium, it can evidently be seen the formation of a heterogeneous protective biofilm-like on the mild steel surface, with marks that resemble those made by Emery SiC paper after polishing (Fig. 13a). Even with heterogeneity, it is possible to observe that the amount of C present in the different regions (Fig. 13b and c) is higher than in polished steel, indicating the formation of a protective film on all surface. By analyzing these areas separately, they also show a significant difference (between them) in relation to the carbon, indicating the formation of a protective multilayer, corroborating the Freundlich theory [100,101,103].





Figure 13. SEM images of mild steel after (a) 5 hours immersed in acid medium with 1.0 g L^{-1} of PDCE and the corresponding EDS data from different areas (b and c)

4. CONCLUSION

Phyllogorgia dilatata crude extract (PDCE) was characterized via LC-HRMS and sixteen organic molecules were identified as its major constituents and it was proved that PDCE acts as a great corrosion inhibitor for mild steel in acid medium. The anticorrosive efficiency increases with the increase in inhibitor concentration and the gravimetric and electrochemical results corroborate each other, reaching an average anticorrosive efficiency of 93.4% at 1 g L⁻¹. PDCE acts as a mixed-type inhibitor (as shown in the polarization curves) and prevents corrosion by adsorbing on the mild steel surface (as seen in the data crossing

between electrochemical and gravimetric measurements). Physical-chemical calculations suggest a chemical adsorption process and SEM with EDS images show the formation of a multilayer protective biofilm-like on the metal surface, confirming that the adsorption process obeys the Freundlich theory.

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