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Assessment of the hydroalcoholic extract and powder cocoa bean shell as corrosion inhibitors for carbon steel in sodium chloride solution

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ABSTRACT

Carbon steel is used in various applications because of its excellent weldability, good mechanical resistance and low cost. However, its application becomes restricted due to its low corrosion resistance in neutral and acidic media, and it is necessary to use processes to retard the corrosive mechanism, such as the use of inhibitors. Many of the effective synthetic inhibitors used are associated with high cost and some have a high toxicity. In recent years, studies of corrosion inhibitors obtained from natural products have been increasing because they are environmentally sustainable and presents low-cost. Therefore, in the present study, different concentrations of the cocoa shell powder (*Theobroma cacao*) and hydroalcoholic extract were evaluated as a corrosion inhibitors of SAE 1008 carbon steel in 0.5 mol.L^{-1} sodium chloride solution. The inhibitory action of the cocoa residue was studied through gravimetric technique and electrochemical impedance spectroscopy (EIS). For the chemical characterization of the inhibitor, the Fourier Transform Infrared Spectroscopy (FTIR) was used. The EIS results showed that the corrosion inhibition efficiency of the steel decreased with the inhibitor concentration, reaching maximum values of 55.97% and 72.93%, for cocoa shell powder and hydroalcoholic extract, respectively. The gravimetric data confirmed the electrochemical results and through the study of the adsorption mechanism it was verified that the adsorbed inhibitor molecules follow the Flory-Huggins isotherm model, for both forms of the inhibitor. For all the concentrations evaluated, the cocoa shell powder did not represent an efficient corrosion inhibitor. In contrast, for the hydroalcoholic extract, at the concentration of 0.44 g.L^{-1}, a good performance was verified as a corrosion inhibitor of SAE 1008 carbon steel in 0.5 mol.L^{-1} sodium chloride solution.

Keywords: Carbon steel, *Theobroma cacao*, Natural Corrosion Inhibitor, EIS, Gravimetric Technique.

1. INTRODUCTION

Carbon steel is widely used in daily life and it has applications in the construction of structures and equipment due to its low temperability, excellent weldability, good mechanical resistance and low cost [1]. Despite these qualities, carbon steel has low corrosion resistance, and processes are needed to provide greater protection against corrosion, such as the use of inhibitors [2].

Corrosion inhibitors are substances or a mixture of substances, which when added in small concentrations to corrosive media, are capable of minimizing the reaction of the metal with the medium. They are able to combat the corrosion process in metals due to the adsorption phenomenon of the ions and organic molecules (especially organic compounds with nitrogen, sulfur and oxygen) on the metal surface, forming a protective layer that promotes the reduction of the reactions between the corrosive medium and the material [3, 4].

Many of the synthetic inhibitors used in industrial systems (such as refinery units, boilers, cooling systems, among others) have good anti-corrosion properties, but they present toxicity and high costs. The toxic components can cause damage to the ecosystem and also to organs of the human body, such as kidneys or liver [3, 4]. The toxicity can manifest itself during the synthesis of the compound or during its application

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and discard. Some practices that exemplify these risks are the use of inhibitors composed of chromium ions and benzotriazole [5-9]. Thus, in recent years, due to the implementation of stricter environmental regulations and also due to the increase in ecological consciousness, the search for alternative solutions to this problem has begun [10]. Then, researchers have intensified their studies on corrosion inhibitors from natural products, which are environmentally friendly and have a low cost [5-11].

Natural inhibitors are obtained through extracts of different parts of plants such as roots, leaves, fruits and flowers [5]. Another way to obtain a green inhibitor was reported by Santos *et al.* [8] whose methodology used to acquire the material is related to the use of the natural product in its powder form (granulometry greater than 170 mesh), where only cleaning and fragmentation of the natural product is carried out. This enables a process of inhibitor obtaining with reduced material resources and time.

The inhibitory properties associated with the green inhibitors are related to the presence of compounds such as flavonoids, alkaloids, tannins, and other natural organic components that have nitrogen, oxygen and sulfur atoms in their molecular structure, which are the active centers for the adsorption process on the metal surface [2-6]. The approach to these inhibitors in the literature usually refers to applications in acidic media [1-9] while studies in neutral media are less common. But, inhibitors are also used in this type of medium. Metallic materials are used in marine environments, particularly in production and transportation industries for the construction of gas pipelines, heat exchangers, cooling water circulation systems and others. Therefore, more research is required in this type of corrosive medium [10, 11].

Some of the studies reported in the literature on the high efficiency of green inhibitors in the protection of carbon steel against corrosion in neutral environments can be highlighted: use of extract of *Myrmecodia Pendans* (parasitic plant found in the forests of the interior of Indonesia) in sodium chloride solution [11] and capsaicin extract from chili pepper in 3.5% NaCl solution [12].

Thus, the inhibitory action of various by-products from industrial processes can be evaluated. In this context about the by-products, it is worth mentioning the southern region of Bahia (Brazil), where there is chocolate manufacturing. One of the residues generated in large quantity in the chocolate production is the cocoa shell, which represents a peel/film that surrounds the cocoa beans. Normally, the cocoa shell is removed from the cocoa bean following the roasting step present in the chocolate production [13, 14]. The cocoa bean shell is composed of pectic polysaccharides, hemicellulose, cellulose, Klason lignin and xanthines (alkaloids), among them theobromine and caffeine, the latter in lower concentrations [15]. Furthermore, the amount and profile of phenolic compounds present in this residue are very significant, therefore, this class of compounds may show antioxidant properties, which can contribute to making this low cost material a more valuable product [16].

Therefore, in the present work, the anticorrosive activity of the cocoa shell (*Theobroma cacao*), in its powder form and hydroalcoholic extract, was evaluated. Thus, the performance of these materials as corrosion inhibitors of SAE (Society of Automotive Engineers) 1008 carbon steel in 0.5 mol.L^{-1} sodium chloride solution was verified, through electrochemical impedance spectroscopy and gravimetric technique (weight loss measurement). The adsorption isotherms were also studied to understand the type of interaction between the molecules present in the inhibitor (adsorbate) and the metallic substrate.

2. MATERIALS AND METHODS

2.1 Obtaining the natural corrosion inhibitor

The cocoa beans shells used were the residues from Riachuelo Farm - Mendoá Chocolates (Highway Ilhéus-Uruçuca, Bahia (Brazil)). This cocoa residue was taken in an oven at a temperature of 70ºC for 6 hours. Afterwards, the shells were crushed in a Marconi ball mill model MA 500. Then, the fragmented material was taken to a Tyler sieve system, coupled to an electromagnetic stirrer, to obtain the powder with maximum particle size of 170 mesh. Thus, it represents the powder corrosion inhibitor to be used.

The cocoa shell powder retained in the sieves prior to 170 mesh (24, 48, 66 and 115 mesh) were used to obtain the hydroalcoholic extract. The cocoa residue was immersed in a hydroalcoholic solution (20% water and 80% ethanol) for 48 hours. And the ratio of mass of powder to mass of solution was 1:10. After a simple filtration, the filtrate was sent to a rotaevaporation system at 50-60°C until the extract was obtained.

2.2 Preparation of carbon steel samples

The metallic substrate used was SAE 1008 carbon steel, supplied by Usiminas - Minas Gerais (Brazil). The composition of the steel by weight is (wt %): C: 0.03; Si: 0.01; Mn: 0.20; P: 0.024; S: 0.013; Al: 0.031; Nb:

0.001; V: 0.001; Ti: 0.001; Cr: 0.01; Ni: 0.01; Sn: 0.001; N: 0.0028; B: 0.0027; Sb: 0.001 and Fe: balance.

In the tests carried out, the samples of carbon steel were cut in the following dimensions: 20 mm x 20 mm x 1 mm and their surfaces were sanded in a politrix model PLF (Fortel brand), using water sands of different granulometries: 80, 120, 320, 400, 600, 1200, 2000 and 2500 mesh. Then, the specimens were washed with distilled water to remove residues from the sandpaper, and then with ethanol and acetone. Finally, the metal surface was dried with hot air.

2.3 Electrochemical techniques

The tests were carried out in an electrochemical cell with three electrode: SAE 1008 carbon steel as a working electrode (with exposed area of 1.0 cm²), Ag|AgCl|KClsat as a reference electrode and a counter electrode of titanium wire coated with rhodium. The electrolyte was a 0.5 mol.L^{-1} NaCl solution. All experiments were done in triplicate, with the solution naturally aerated and at 25°C.

The electrochemical measurements of the samples in the presence and absence (blank) of inhibitor were obtained in a Metrohm Autolab potentiostat/galvanostat, model PGSTAT302N with software NOVA 1.11 and for data treatment the Microcal Origin 8.0 software was used. Five different concentrations of cocoa shell powder and hydroalcoholic extract were studied: 0.44 g.L^{-1}, 0.77 g.L^{-1}, 1.11 g.L^{-1}, 1.44 g.L^{-1} and 1.77 g.L^{-1}. The concentrations values were based on the research of BARRETO *et al.* [7] and SANTOS *et al.* [8].

Initially, the open circuit potential (OCP) test was carried out for 90 min in order to stabilize the corrosion potential (E_{corr}). This stabilization time was used according to BARRETO *et al.* [7] and SANTOS *et al.* [8, 17] methodologies. Subsequently, electrochemical impedance spectroscopy (EIS) measurements were performed, using a frequency range of 100 kHz to 10 mHz with 10 points/decade and amplitude of 10 mV (rms) and after that, the anodic and cathodic polarization curves were obtained from -30 mV to +250 mV *vs* OCP and -250 mV to +30 mV *vs* OCP, respectively. For quantitative analyzes, the EIS results were fitted using Zview software.

2.4 Gravimetric tests

The gravimetric tests were performed according to the ASTM G1-03 standard [18]. The carbon steel samples were sanded, washed and dried with hot air, as previously described (item 2.2). Afterwards, the mass of the steel samples ($m_{initial}$) was measured using an analytical balance with 0.1 mg precision (Marte Científica and model AY220). Subsequently, they were immersed in 0.5 mol.L^{-1} NaCl aqueous solution, in the absence and presence of different concentrations of the inhibitor for 2 h. After that, the acid pickling of the sample was carried out with immersion in 0.5 mol.L^{-1} HCl solution during 5 min. Subsequently, the samples were washed with distilled water, cleaned with a brush and washed with ethanol and acetone. Afterwards, they were dried with hot air, and then their mass was measured to verify the mass loss (m_{final}).

Furthermore, a gravimetric pickling test was carried out in order to verify if acid pickling had not attacked the base metal. Thus, to correct the mass loss of carbon steel, the sample (blank) was immersed in the pickling solution (HCl 0.5 mol.L^{-1}), for 5 min in the absence of inhibitor and without immersing previously in the NaCl solution. Using an analytical balance, the mass of the steel was measured before ($m_{blank\ initial}$) and after ($m_{blank\ final}$) immersion in the pickling solution. The calculation of the weight loss correction of the base metal was performed according to equation (1):

$$C_R = \frac{\left(m_{initial} - m_{final}\right) - \left(m_{blankinitial} - m_{blankfinal}\right)}{s \times t} \tag{1}$$

Where: C_R is the corrosion rate, expressed in g.cm^{-2}.s^{-1}; $m_{initial}$ is the mass of the sample before immersion (expressed in g); m_{final} is the mass of the specimen after pickling; $m_{blank\ initial}$ corresponds to the mass of the sample (blank) before pickling (in g), $m_{blank\ final}$ represents the mass of the test sample (blank) after pickling; *s* is the exposed area to the corrosive medium (in cm^2) and *t* is the immersion time, expressed in seconds.

2.5 Chemical characterization

The inhibitor chemical characterization was performed by Fourier Transform Infrared Spectroscopy (FTIR) to identify the functional groups present in in the cocoa shell powder and hydroalcoholic extract. The analysis were carried out using a spectrophotometer from Thermo Scientific Nicolet, model iS10 by ATR (Attenuated Total Reflectance), in the range of 4000 to 650 cm^{-1} and a resolution of 4 cm^{-1}.

2.6 Metal surface characterization

In order to perform the morphological surface analysis, the samples of SAE 1008 carbon steel were sanded in the same granulometries used for the other tests (electrochemical and gravimetric). Afterwards, the samples were washed with alcohol and acetone and dried in a stream of hot air and then the gravimetric tests were carried out (item 2.4).

After these tests, the carbon steel samples were washed with distilled water and dried, and then their surfaces were analyzed by the Leica S9 stereo microscope. The software used to acquire images from the microscope was the Leica Application Suite. The steel samples were evaluated before immersion in the electrolyte and also in the presence and absence of inhibitor in the NaCl solution.

3. RESULTS AND DISCUSSION

3.1 Chemical characterization

The FTIR spectra obtained for the cocoa shell powder (Po) and hydroalcoholic extract (Ex) can be observed in Figure 1. Table 1 presents the possible bands and functional groups identified in these inhibitors.

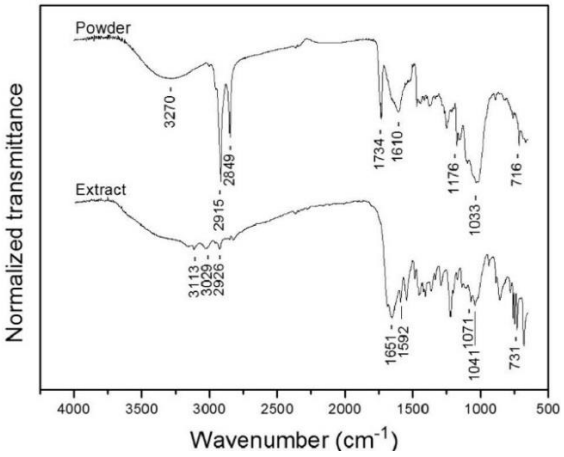


Figure 1: Spectra FTIR the cocoa shell powder and hydroalcoholic extract.

Table 1: Bands and functional groups identified in the inhibitors [15, 19, 20].

WAVENUMBER (cm^{-1})	FUNCTIONAL GROUP
3600 – 3200	O-H
3500 – 3100	N-H
3000 – 2850	C-H alkanes (stretching)
2900 – 2800	C-H (aldehyde)
1760 – 1690	C=O
1620 –1400	C=C
1300 – 1000	C-O
1350 – 1000	C-N
1690 – 1640	C=N
900 – 690	C-H aromatic (out-of-plane)

Figure 1 shows that there are some similarities between the spectra, but some peaks differ due to the stretching and intensities of the bands, resulting in a greater presence of compounds in the extract.

The absorption band between 3270 cm^{-1} and 3029 cm^{-1}, can be attributed to the axial deformation of O-H or the N-H group. The cocoa shell has phenolic compounds, lignin, hemicellulose, cellulose and fatty acids, in which the hydroxyl group (OH) is present. The N-H bonds may be present due to the alkaloids of the cocoa residue, such as: theobromine and caffeine [16, 19].

The bands in the region between 2915 cm^{-1} and 2849 cm^{-1}, indicated by the presence of alkane groups and aldehyde groups, respectively, can also be observed. PUA *et al.* [20] studied the cocoa pod husk and

found peaks very close to them, related to the C-H binding stretching in cellulose and hemicellulose. The presence of these components was already expected for the cocoa shell, since, according to AHMAD *et al.* [15], this residue has approximately 35% of cellulose and 20% of hemicellulose.

The band in the 1734 cm^{-1} region can be related to the C=O bonds present in the aromatic rings of lignin and the saturated fatty acids present in the cocoa residue. The presence of bands at 1033 cm^{-1} and 1176 cm^{-1}, for cocoa shell powder, and 1071 cm^{-1} and 1041 cm^{-1} for extract, can be ascribed to the C-O or C-N groups [15, 20].

Furthermore, in the cocoa shell powder, the band at 1610 cm^{-1} is attributed to the stretching vibration of the C=C double bonds, which are related to the presence of lignin and aromatic compounds from the flavonoids of the cocoa shell. For the extract, the C=C bonds of the aromatic bonds may be associated in the region of 1651 cm^{-1}. Moreover, this same region may also indicate the C = N bonds present in theobromine and caffeine [21, 22]. In the region of 1651 to 1592 cm^{-1} the band may correspond to the vibration of the H-O-H flexion that is related to the absorbed water molecules [23]. Water molecules may be present because it was probably not possible to eliminate them completely during the extraction process. This can provide a higher polarity in the extract.

In the spectrum of the extract, the bands related to the aromatic bond were observed at 731 cm^{-1}, attributed to angular deformation of C-H of aromatic bond. However, for the cocoa shell powder, the aromatic bond can be observed at 716 cm^{-1} [22, 24].

Thus, functional groups with heteroatoms (oxygen and nitrogen) and double bonds (C=O, C=C and C=N) were observed in the spectrum for the cocoa shell powder and extract. According to ROCHA *et al.* [4], the presence of organic compounds containing nitrogen, oxygen, sulfur and double or triple bonds facilitates their adsorption on the metal surface, forming a protective barrier that minimizes the corrosive process.

3.2 Gravimetric tests

The gravimetric tests were carried out on SAE 1008 carbon steel samples immersed during 120 min in NaCl 0.5 $mol.L^{-1}$, in presence and absence of different inhibitor concentrations. After this immersion time, a pickling was performed, in the case of powder, because for the extract it was not necessary to pickle.

The corrosion rate was calculated according to equation (1) and the inhibition efficiency (η), in percentage (%), was calculated according to equation (2). Through this parameter, it is also calculated the degree of metallic surface coverage (θ= η/100) [25].

$$\eta = \frac{C^0{}_R - C_R}{C^0{}_R} \times 100 \tag{2}$$

Where: $C_R{}^0$ is corrosion rate in the absence of the inhibitor and C_R is the corrosion rate in the presence of the inhibitor [25].

The corrosion current density (i_{corr}), expressed in equation (3), was also calculated:

$$i_{corr} = C_R \frac{96500}{E_{qmetal}} \tag{3}$$

Where: 96500 $C.mol^{-1}$ represents the value of the Faraday's constant and E_{qmetal} is the equivalent-gram of the electrode used. In this research, the work electrode is carbon steel, whose value was 27.93 g, corresponding to pure iron [26].

Table 2 shows the parameters calculated by the gravimetric tests associated with the standard deviation values. Through the gravimetric results it is possible to observed the inhibition efficiency decreases with increasing inhibitor concentration. Thus, for both forms of inhibitor, a higher efficiency is observed for 0.44 $g.L^{-1}$ (lowest concentration), which can be attributed to the adsorption mode of the inhibitor [27-29]. When the inhibitor concentration is 0.44 $g.L^{-1}$, the cocoa shell powder and extract molecules adsorb in the active sites parallel to the electrode surface. According to ZENG *et al.* [27], in such situations, with the additional increase in the inhibitor concentration, the molecules may mutually repulse because, in higher concentrations, the inhibitory molecules tend to perpendicularly adsorb on the carbon steel surface due to the electrostatic repulsive effect. When compared with paralleled adsorption, the inhibitory molecule adsorbed with perpendicular adsorption occupies a smaller surface area which results in a decrease in inhibition efficiency [28-30].

For the cocoa shell powder, at the studied concentrations, the corrosion inhibition efficiency is lower

than 70% demonstrating a low performance as corrosion inhibitor. Because, according to classic literature, the corrosion inhibition efficiency must be greater than 70% for an inhibitor to be classified as efficient [31]. This is related to the low surface coverage (θ less than 0.585) through the adsorbed inhibitors molecules, so the barrier layer formed is not enough to protect the steel surface [32]. Although it does not form a barrier that provides high values of inhibition efficiency, it is verified that, with the presence of the cocoa shell powder, there is a lower corrosion rate and a lower current density, when compared to the condition without inhibitor. But this difference is not significant and therefore, the cocoa shell powder does not represent an efficient corrosion inhibitor in the evaluated conditions.

Table 2: Results of gravimetric tests in 0.5 mol.L^{-1} NaCl.

INHIBITOR FORM	CONCENTRATION OF INHIBITOR (C) (g.L^{-1})	C_R (g.cm^{-2}.h^{-1})	i_{corr} (A.cm^{-2})	Θ	η (%)
Cocoa Shell Powder	Blank	(8.70 ± 0.79) x 10^{-5}	(8.36 ± 0.76) x 10^{-5}	-	-
	0.44	(2.29 ± 0.03) x 10^{-5}	(2.20 ± 0.03) x 10^{-5}	0.585 ± 0.004	58.48 ± 0.36
	0.77	(3.64 ± 0.05) x 10^{-5}	(3.49 ± 0.04) x 10^{-5}	0.554 ± 0.005	55.45 ± 0.52
	1.11	(4.47 ± 0.05) x 10^{-5}	(4.29 ± 0.05) x 10^{-5}	0.543 ± 0.006	54.35 ± 0.57
	1.44	(4.24 ± 0.22) x 10^{-5}	(4.07 ± 0.21) x 10^{-5}	0.512 ± 0.018	51.25 ± 1.79
	1.77	(5.05 ± 0.37) x 10^{-5}	(4.84 ± 0.36) x 10^{-5}	0.419 ± 0.043	41.93 ± 4.29
Hydroalcoholic Extract	0.44	(4.92 ± 0.22) x 10^{-7}	(4.73 ± 0.21) x 10^{-7}	0.766 ± 0.010	76.61 ± 1.02
	0.77	(6.65 ± 0.25) x 10^{-7}	(6.38 ± 0.24) x 10^{-7}	0.684 ± 0.012	68.41 ± 1.20
	1.11	(8.99 ± 0.26) x 10^{-7}	(8.63 ± 0.25) x 10^{-7}	0.573 ± 0.012	57.28 ± 1.21
	1.44	(9.68 ± 0.52) x 10^{-7}	(9.29 ± 0.49) x 10^{-7}	0.540 ± 0.025	54.04 ± 2.45
	1.77	(1.18 ± 0.08) x 10^{-6}	(1.13 ± 0.07) x 10^{-6}	0.441 ± 0.037	44.12 ± 3.71

On the other hand, for the hydroalcoholic extract, at the concentration of 0.44 g.L^{-1}, the corrosion inhibition efficiency was greater than 70%. Furthermore, for this condition, the lowest values of corrosion rate and corrosion current density were observed. Although obtaining the extract requires a greater number of production steps and more time, when compared to the powder form, in 0.44 g.L^{-1} of extract is verified a good performance as corrosion inhibitor of SAE 1008 carbon steel in 0.5 mol.L^{-1} sodium chloride solution.

The difference in the corrosion inhibition efficiency of the extract and the cocoa shell powder may be related to a variety of factors that encompass the presence of the functional groups and elongation of the bands and intensities, as observed in the FTIR spectra (Figure 1). Furthermore, the extract may have a greater presence of polar groups collaborating in the inhibitory characteristics. According to RANI and BASU [6], the polar group present in the compounds acts as the reaction center for the adsorption process of the molecules.

3.3 Adsorption isotherm

The data adjustment obtained in different concentrations were performed in the adsorption isotherms models to aid the understanding of the interactions between the adsorbate and the substrate.

According to the five inhibitor concentrations and the data of the metallic surface coverage degree (Table 2), the adsorption isotherms adjustments were tested in different models as Langmuir, Freundlich, Temkin, Frumkin and Flory-Huggins. Through this study, it is possible to understand the interactions between the adsorbate and the substrate surface. The adsorption parameters obtained through the straight-line equations, resulting from the adjustment of the experimental data to the isotherm models, and their correlation coefficient (R^2) are presented in Table 3.

Table 3: Adsorption parameters obtained in the isotherms models for the corrosion inhibition of SAE 1008 carbon steel in NaCl.

INHIBITOR FORM	ADSORPTION ISOTHERMS	R²	STRAIGHT-LINE EQUATION
Cocoa Shell Powder	Langmuir (C/θ versus C)	0.9799	- 0.719 + 2.666x
	Freundlich (log θ versus log C)	0.9102	- 0.269 - 0.327x
	Temkin (θ versus log C)	0.9413	- 40.850 - 54.534x
	Flory-Huggins (log(θ /C) versus log (1- θ))	0.9909	- 1.402 - 3.226x
	Frumkin (log (θ/(1-θ).C) versus θ)	0.9787	4.087 - 2.147x

Hydroalcoholic Extract	Langmuir (C/θ versus C)	0.9731	- 0.732 + 2.527x
	Freundlich (log θ versus log C)	0.9293	- 0.231 - 0.375x
	Temkin (θ versus log C)	0.9625	0.599 - 0.520x
	Flory-Huggins (log(θ /C) versus log (1- θ))	0.9936	- 1.150 - 2.212x
	Frumkin (log (θ/(1-θ).C) versus θ)	0.9862	3.745 - 2.058x

The Flory-Huggins isotherm considers that an active site can accommodate more than one molecule or one single molecule can adsorb in more than one site [33]. The adsorption phenomenon of the corrosion inhibiting molecules for this model can be represented by the following equation [34]:

$$\log(\theta / C) = \log K + x\log(1-\theta) \tag{4}$$

Where: θ is the surface coverage degree, C is the inhibitor concentration, K is the equilibrium constant of the inhibitor adsorption process, and x represents the number of adsorbed water molecules, which are replaced by the inhibitor molecules [34].

The angular coefficients to the Flory-Huggins model (Table 3) are less than 1 (values equal to -3.226 and - 2.212 corresponding, respectively, to the cocoa shell powder and ethanolic extract) indicating that the organic molecule was not efficiently adsorbed on the metal surface, which possibly explains the fact that high values of corrosion inhibition efficiency were not observed, as verified in the gravimetric technique. According to MOTAMEDI *et al.* [33], when the angular coefficient of the straight-line equation for this model is higher than 1, it indicates that one inhibitor molecule substitute more than one active site on steel surface.

From the adjustment of the Flory-Huggins isotherm model, it is possible to calculate the adsorption constant (K) according to the line equation expressed in the graph shown in Figure 2.

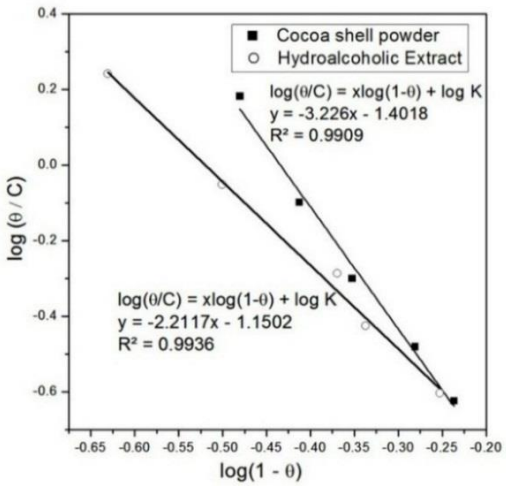


Figure 2: Flory-Huggins adsorption plots for the SAE 1008 carbon steel for different concentrations of cocoa shell powder and hydroalcoholic extract in 0.5 mol.L^{-1} NaCl.

The linear coefficient of Flory-Huggins for cocoa shell powder is equal to -1.4018 and for the extract the value is -1.1502. These coefficients correspond to log K, then the adsorption constants values are 0.03965 L.g^{-1} and 0.07079 L.g^{-1}. From this constant and considering a temperature of 298 K in the equation (5), it can be calculating the adsorption free energy of Gibbs (ΔG^{o}_{ads}) [34]:

$$\Delta G^{o}_{ads} = -RT\ln(C_{H2O}.K) \tag{5}$$

Where: T is the absolute temperature (whose value in this study is 298 K), R is the universal gas constant (8.3147 J.mol^{-1}.K^{-1}), C_{H2O} is the concentration of water (55.5 in mol.L^{-1} or 1000 in g.L^{-1}) [34, 35].

Thus, the adsorption free energy of Gibbs is -9.118 kJ.mol^{-1} for the inhibitor in the powder form and -10.555 kJ.mol^{-1} for the extract. Both values indicate that the adsorption process of the organic molecules on the carbon steel surface occurs spontaneously due to its negative number [33, 36].

The Gibbs adsorption free energy value also indicates the type of adsorption, and these values are less negatives than -20 kJ.mol^{-1}, which corresponds a physisorption [33-36]. The physical adsorption phenomenon

occurs due to a weak electrostatic attraction between the charged metal surface and the charged inhibitory molecules [1, 8].

Thus, the inhibitory molecules present in the cocoa shell powder and hydroalcoholic extract were physically adsorbed on the carbon steel surface. Therefore, adsorbed molecules are able to hindering the charges exchange between carbon steel and electrolyte, that is to say, they hinder the corrosion process.

3.4 Electrochemical techniques

3.4.1 Electrochemical impedance spectroscopy (EIS)

The EIS measurements were performed after 90 min of the open circuit potential stabilization. Figure 3 presents the Nyquist (a), (c) and Bode plots (phase angle (b), (d)) obtained for SAE 1008 carbon steel in 0.5 mol.L^{-1} NaCl solution in absence (blank) and in the presence of different concentrations of the inhibitor, in the form of cocoa shell powder and hydroalcoholic extract.

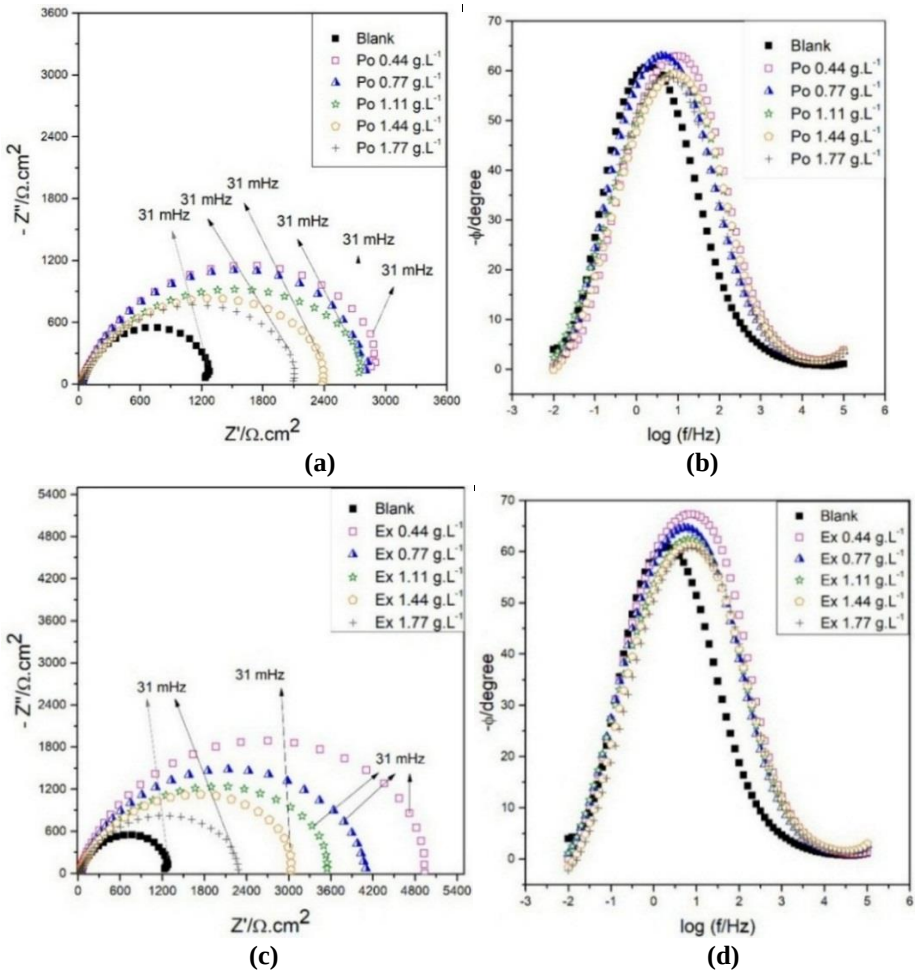


Figure 3: Nyquist and Bode plots (containing the phase angle) for the carbon steel in the absence and presence of different concentrations of the cocoa shell powder (a), (b), respectively, and hydroalcoholic extract (c), (d), in NaCl 0.5 mol.L^{1}.

The Nyquist diagrams (Figures 3 (a), (b)) show that the curves shape is not affected by the presence of the inhibitor, which indicates, according to MOURYA *et al.* [25], that there is no change in the corrosion mechanism. In addition, it may also be noted that for both powder and the extract, with increasing inhibitor concentration, there is a decrease in the diameter of the semicircles of the diagram, which results in a corrosion resistance reduction. This behavior can be attributed to the adsorption mode of the inhibitor. In the lowest concentration of cocoa shell powder and also of extract (0.44 g.L^{-1}), the adsorption of the molecules can be assumed that was parallel to the metal surface, so these molecules occupied a greater area on the surface, consequently, more active corrosion sites were blocked, providing greater resistance to corrosion. However,

with increasing concentration, the molecules repelled, so that inhibitory molecules tended to adsorb perpendicularly to the carbon steel surface due to the electrostatic repellent function that occupies a small area on the metal surface, which results in a decrease in corrosion resistance [27-29].

In most of the studies reported in the literature on corrosion inhibitors in NaCl solution, an increase in corrosion resistance is reported as the concentration of the inhibitor is increased [11, 32, 37]. However, in some studies on the efficiency of corrosion inhibition with different concentrations of inhibitor, it has been observed that there is an ideal inhibitor concentration. Some researchers have observed that the inhibition efficiency has increased to a certain inhibitor concentration. But, with the additional increase in concentration, reaching a value higher than the optimal inhibitor concentration, a reduction in inhibition efficiency started [27, 28]. In these studies, the peak-value-phenomenon was presented, which may be associated with the adsorption mode of the inhibitor. In the same way, the researchers found that, with the additional increase in the inhibitor concentration, the molecules may mutually repulse, causing a reduction in the corrosion rate [28-30].

In the Bode plots (Figure 3 (b) and (d)) are observed that the smaller phase angles are presented for the highest concentrations evaluated. In addition, only one time constant is verified [8]. In Figure 3 (b) and (d)), when comparing with blank, it is noted that, at the lowest concentrations of inhibitor, there is a more pronounced displacement at high frequencies. According to RIBEIRO and ABRANTES [38], the region of high frequency is characterized by the presence of a superficial cover, which can be attributed to the parallel adsorption of the inhibitory molecules at the metal-solution interface [29, 30].

A quantitative analysis of the addition effects of the cocoa shell powder and hydroalcoholic extract on the corrosion resistance of the SAE 1008 carbon steel was evaluated. It was performed a correlation of the impedance data (Figure 3) with an equivalent circuit, whose model used is presented in Figure 4. This circuit has also been used in different studies reported in the literature on natural inhibitors applied in the protection of carbon steel in sodium chloride media [11, 32, 37]. Using the Z-View software, the experimental data were fitted to the equivalent circuit, which represents a parallel combination of the charge transfer resistance (R_{ct}) and the electrical double layer capacitance considering the introduction of the constant phase element (CPE_{dl}), both in series with the solution resistance (R_s). Thus, R_s represents the ohmic resistance of the electrolyte and R_{ct} is a measure of the electric charge transfer through the metal/solution interface. R_{ct} is equivalent to the polarization resistance and its value is inversely proportional to the corrosion rate [38].

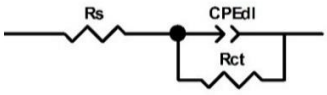


Figure 4: Electrical equivalent circuit used to adjust the EIS diagrams.

Through the charge transfer resistance it is possible to calculate the efficiency of the corrosion inhibitors (η_{wL}), as presented in equation (6) [4]:

$$\eta_{WL} = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \tag{6}$$

Where: $R_{ct,0}$ is the charge transfer resistance in the absence of inhibitor (blank) and R_{ct} represents the charge transfer resistance in the presence of the inhibitor [4].

The constant phase element is introduced into the circuit instead of the pure capacitor of the electrical double layer to compensate for the deviations from the ideal behavior, providing greater precision to the data fit [39]. These deviations are observed in the imperfect semicircles in Nyquist plots. And they are related to the surface inhomogeneity, roughness, electrode porosity or frequency dispersion of the interfacial impedance [4, 9, 39]. The impedance of CPE (Z_{CPE}) is expressed according to equation (7) [40]:

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-n} \tag{7}$$

Where: Y_0 is the CPE value; ω is the angular frequency; j^2 is the imaginary number and it is equivalent to -1, and *n* provides information on the homogeneity of the surface [40]. Some values of *n* are simplified for discrete elements, such as α values, which is the dispersion factor. When this value is equal to 1, it refers to a pure capacitor and its behavior is that of an ideal electrode [2].

Through the fit to the electrical equivalent circuit some electrochemical parameters were obtained and are presented in Table 4. Figure 5 shows a good agreement between experimental and fitted results for the hydroalcoholic extract at 0.44 g.L^{-1} concentration, which were similar for the same powder concentration and for the other concentrations in the powder and hydroalcoholic extract. The quality of the fitted data was expressed by χ^2 (chi-squared).

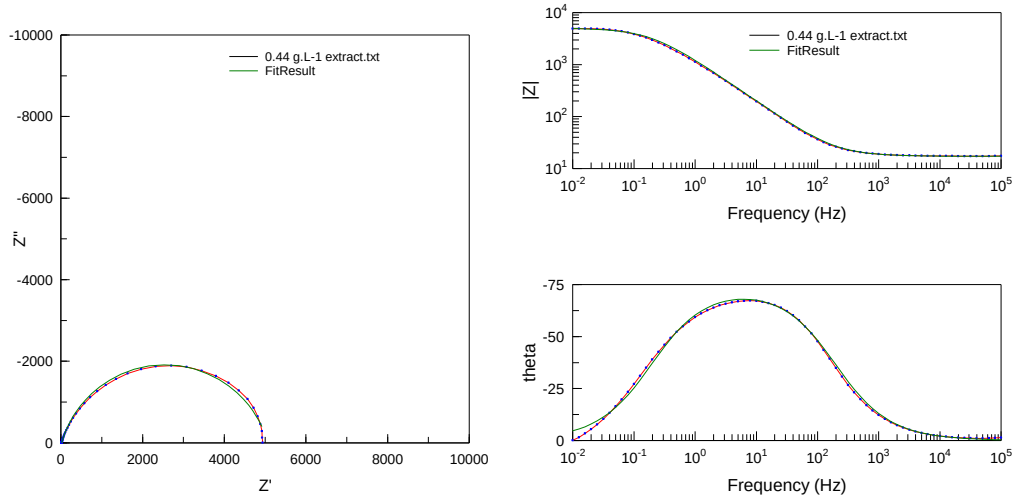


Figure 5: Fit in the Z-View software of experimental data (Nyquist (a) and Bode plots (b)) for 0.44 g. L^{-1} hydroalcoholic extract in 0.5 mol.L^{-1} NaCl.

Table 4: Electrochemical parameters obtained through electrical equivalent circuit.

INHIBITOR FORM	CONCENTRATION OF INHIBITOR (C) (g.L^{-1})	R_S (Ω.cm²)	R_{CT} (Ω.cm²)	CPE_{dl} (μFcm^{-2}s$^{(α-1)}$)	α	χ^2	INHIBITION EFFICIENCY (%)
Cocoa Shell Powder	Blank	19.33	1373	6.83 x 10^{-4}	0.82	8.05 x 10^{-3}	-
	0.44	21.73	3118	2.84 x 10^{-4}	0.79	1.83 x 10^{-3}	55.97
	0.77	22.63	2981	2.80 x 10^{-4}	0.80	2.29 x 10^{-3}	53.94
	1.11	22.52	2809	2.55 x 10^{-4}	0.76	2.47 x 10^{-3}	51.12
	1.44	23.44	2441	2.27 x 10^{-4}	0.77	2.37 x 10^{-3}	43.75
	1.77	22.36	2205	3.20 x 10^{-4}	0.77	1.63 x 10^{-3}	37.73
Hydroalcoholic Extract	0.44	17.20	5050	1.66 x 10^{-4}	0.82	4.69 x 10^{-3}	72.81
	0.77	20.91	4130	2.30 x 10^{-4}	0.80	8.98 x 10^{-4}	66.76
	1.11	20.40	3618	2.48 x 10^{-4}	0.78	1.84 x 10^{-3}	62.05
	1.44	21.03	3238	2.32 x 10^{-4}	0.77	9.50 x 10^{-4}	57.60
	1.77	18.27	2370	2.55 x 10^{-4}	0.78	7.76 x 10^{-4}	42.08

The values of χ^2 (Table 4) are less than 8.05 x 10^{-3}. This shows that the fitted data from the equivalent circuit used have a good agreement with the experimental data, because, MOURYA *et al.* [25] and OSÓRIO *et al.* [41], obtained in their research chi-squared values less than 9.00 x 10^{-3} and they stated that the results indicated a good fitting to the proposed circuit.

The values for the dispersion factor (α) are in the range of 0.76 to 0.82, demonstrating non-ideal capacitive behavior. According to MAHDAVIAN and ATTAR [37] and YURT *et al.* [42], this parameter is related to the heterogeneity of the surface and the lower its value, the more heterogeneous the surface. Thus, a more heterogeneous surface was verified, which may be related to the absence of uniformity in the adsorption process of the inhibitory molecules.

Furthermore, it is found that the charge transfer resistance (R_{ct}) decreases with increasing inhibitor concentration. For both conditions of inhibitor, the highest value of R_{ct} is observed at the concentration of 0.44 g.L^{-1}, in which there is saturation of the inhibitory molecules on the metal surface, indicating that the inhibitor forms a layer that serves as a barrier, minimizing the charge transfer.

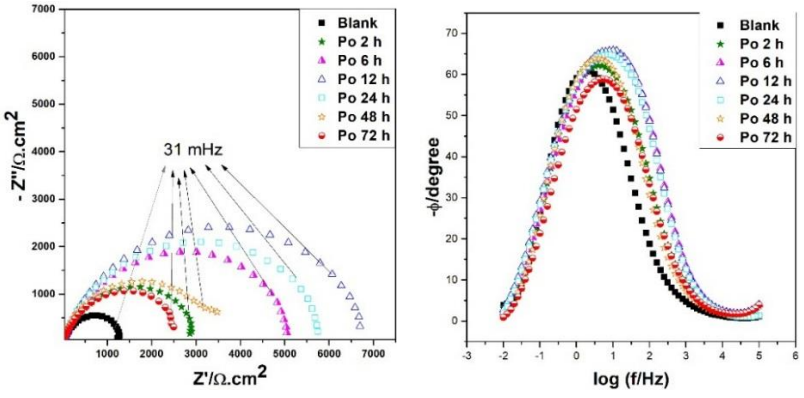
Table 4 also shows the electrical double layer capacitance values considering the introduction of the constant phase element (CPE_{dl}). The literature reports that the CPE_{dl} values follow the opposite direction of the R_{ct} values, being related to the decrease of the dielectric constant or the increase of double layer thickness, suggesting a strong adsorption of the molecules on the metal surface [11, 32]. However, in the results of the present study, this effect is not pronounced in this way, and a variation of CPE_{dl} is observed as the concentration increases. Possibly it may be a consequence of the fact that the inhibitory molecules adsorbed at the metal-solution interface were not sufficient to considerably modify the structure of the electrical double layer, which may also be related to not very high values of corrosion inhibition efficiency.

The electrochemical results corroborate the gravimetric results. The concentration of 0.44 $g.L^{-1}$ presents the best condition for corrosion protection for both forms of inhibitor, it is observed that, for the cocoa shell powder, the efficiency is 55.97% and for the extract, this value is equivalent to 72.93%. Thus, for this concentration, the extract can be considered an effective inhibitor in NaCl, since the classic literature declares 70% as the minimum value of efficiency for which an inhibitor is considered efficient in its protection against corrosion [31]. The other concentrations of inhibitor were effective in protecting the metal surface, but the adsorbed molecules were not sufficient to form a protective barrier that provides high inhibition efficiencies.

EIS measurements by immersion time were performed for the inhibitor concentration that presented the best impedance value (Figure 3) to better understand the inhibitor mechanism action on the steel corrosion resistance.The EIS immersion time was performed for sample with 0.44 $g.L^{-1}$ inhibitor after 2, 6, 12, 24, 48 and 72 h of immersion in 0.5 $mol.L^{-1}$ NaCl as presented in Figure 6. And Figure 7 shows the corrosion inhibitor efficiency (calculated with equation 6) at different immersion times.

Figures 6 (a) and (b) show that, for the cocoa shell powder, from 2 to 12 hours, there is an increase in phase angle and electrochemical impedance values, which is due to the adsorption of inhibitory molecules, whose phenomenon in the initial 12 hours it forms a denser protective layer, performing well on corrosion inhibition efficiency, as can be confirmed in Figure 7 [43]. After 12 hours of immersion there is a decrease in electrochemical impedance, so after this period a reduction in inhibition efficiency is observed (Figure 7). JI *et al.* [44] consider that the time in which the reduction of the corrosion resistance begins corresponds to a period in which there is saturation of the inhibitory molecules that are adsorbed, then, after a certain period, these molecules are not able to limit the access of the ions chloride through the protective barrier layer formed at the metal-solution interface. Then, for this study, the immersion of 12 hours represents the saturation time.

It is also noteworthy that the reduction in efficiency in relation to the increase of the immersion time is consistent with the type of adsorption mechanism in the system, which is the physisorption, as verified by equation 5. Physical adsorption involves weak forces, thus over time, a gradual desorption process possibly occurs, consequently the corrosion inhibition efficiency decreases after long periods of immersion.



(a) **(b)**

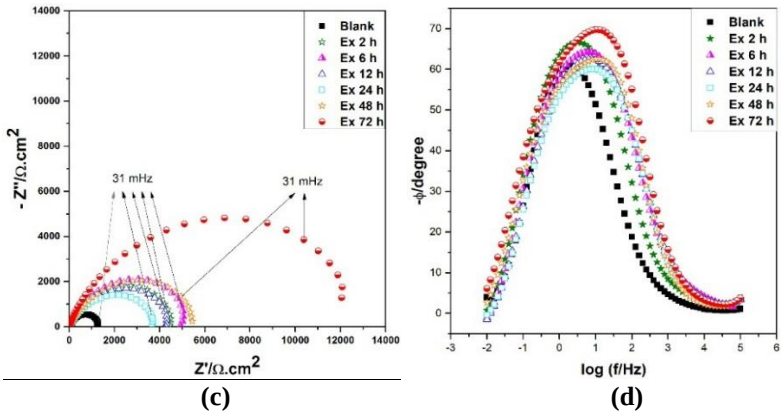


Figure 6: Nyquist and Bode plots (containing the phase angle) for the carbon steel in the presence of 0.44 $g.L^{-1}$ of the cocoa shell powder (a), (b), respectively, and hydroalcoholic extract (c), (d), for different immersion times in 0.5 $mol.L^{-1}$ NaCl.

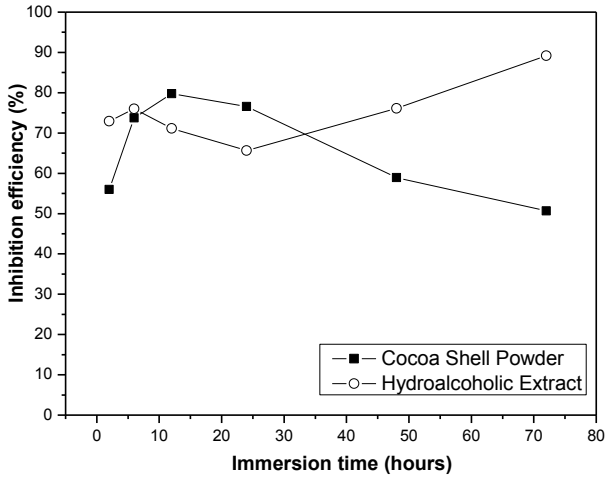


Figure 7: Corrosion inhibition efficiency at different immersion times in 0.5 $mol.L^{-1}$ NaCl solution.

For the extract it is verified that in 12 hours of immersion a reduction in the impedance value occurs, indicating a decrease of the efficiency of action of the inhibitor (Figure 7). On the other hand, an increase in impedance is observed in 48 and 72 hours, for the hydroalcoholic extract (Figure 6 (c)), verifying that in 72 hours the increase is even more discrepant. This is probably occur due to impedance measured is related to the corrosion product already formed, since after 6 hours the carbon steel sample had already undergone a strong corrosive attack. Thus, after 12 hours and 6 hours, for the cocoa shell powder and extract, respectively, the organic molecules that adsorb at the surface lose their inhibitory effect and also the desorption process begins [8, 17, 45]. This shows that both inhibitors studied are not indicated for use in long periods of immersion.

3.4.2 Potentiodynamic polarization curves

The potentiodynamic polarization curves were obtained after 105 min of immersion in the electrolyte, after OCP and EIS measurements. The anodic and cathodic polarization curves, in the absence and presence of different concentrations of hydroalcoholic extract, are presented in Figure 8 (a) and (b), respectively, and cocoa shell powder, are presented in Figure 8 (c) and (d).

Figures 8 (a) and (b) show that the current densities have very close values when scanning potential to higher potentials. However, in the region around E_{corr}, the values of the current densities (especially in the anodic branch) decreased in the presence of hydroalcoholic extract. This suggests that the addition of the extract inhibits both the anodic metal dissolution and the cathodic reaction (oxygen reduction). Therefore, this inhibitor can be considered as a mixed type inhibitor. According to ITUEN *et al.* [9], classifying an inhibitor as mixed type means that it inhibits the corrosion process by geometric blocking of both cathodic and anodic surface active sites. Studies reported in the literature on natural corrosion inhibitors in sodium chloride media also considered the researched extracts within this classification [11, 12, 46].

In Figure 8 (c) it is evident that the cocoa bean shell powder is inefficient to block the anodic reactions that occur in carbon steel, thus observing small changes when compared to the blank curve. On the other hand, in Figure 8 (d), it is observed that the cathodic current densities decreased, indicating a mostly cathodic behavior of the powder.

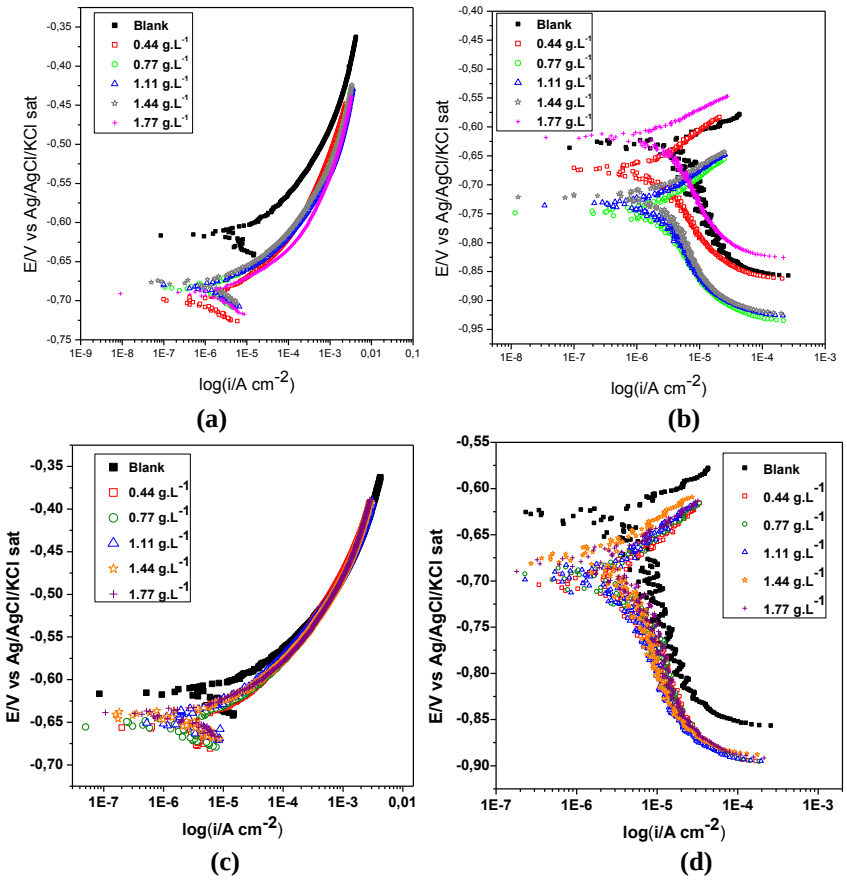
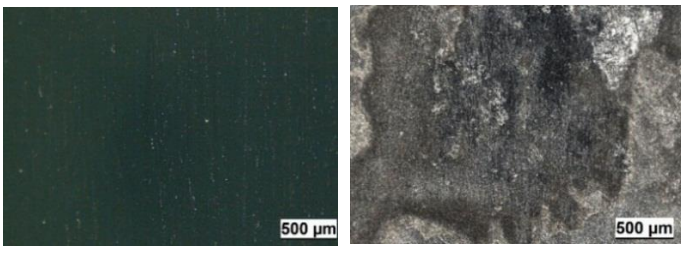


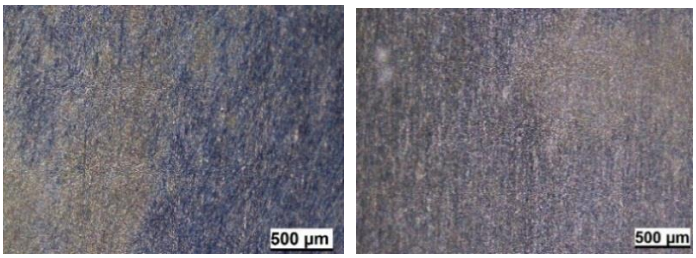
Figure 8: Anodic (a) and Cathodic (b) curves for SAE 1008 carbon steel in 0.5 mol.L^{-1} NaCl solution in the absence and presence of different concentrations of hydroalcoholic extract and for the cocoa shell powder, Anodic (c) and Cathodic (d) curves.

However, it is important to note that, in the presence of both the cocoa shell powder and the extract, the corrosion potentials were shifted compared to the blank measurement. But, in none of the cases studied, this displacement exceeded 85 mV. According to ITUEN *et al.* [9] and EL-LATEEF *et al.* [47], the classification of inhibitors as cathodic or anodic only is feasible only in situations whose potential displacement is at least 85 mV with respect to system measurement in the absence of the inhibitor (blank). Therefore, the present evaluated cocoa residues will be classified as mixed type inhibitors.

3.5 Morphological characterization

The morphological characterization images were obtained by optical microscopy (OM) after the gravimetric tests carried out for 2h of immersion in 0.5 mol.L^{-1} NaCl. The images are show in Figure 9.





(c) **(d)**

Figure 9: Surface of SAE 1008 carbon steel before immersion (a), after 2 hours of immersion in 0.5 mol.L^{-1} NaCl solution in the absence of inhibitor (b), in the presence of 0.44 g.L^{-1} of cocoa shell powder (c) and in the presence of 0.44 g.L^{-1} of hydroalcoholic extract (d).

Figure 9 (a) shows the surface of sanded carbon steel before immersion in NaCl, exhibiting the scratches produced by the abrasion of the sandpapers used. Figure 9 (b) presents the corrosive attack on the carbon steel after 2 hours of immersion in the electrolyte, in the absence of the inhibitor, observing the surface completely covered with corrosion products.

Figure 9 (c) shows the morphology of the metal surface, after immersion in the electrolyte, in the presence of 0.44 g.L^{-1} of cocoa shell powder. In the presence of this inhibitor, a corroded area is observed, indicating the inhibitor molecules are not homogeneously adsorbed in the surface, then it not sufficiently effective to prevent the electrolyte attack on the substrate surface [12], however it is able to reduce the corrosion process when compared with the attacked substrate without inhibitor (Figure 9 (b)).

On the other hand, in the presence of the extract (Figure 9 (d)), a less attacked surface is observed than in the presence of powder (Figure 9 (c)), being also verified a smaller quantity of corrosion products. In addition, a comparison between Figures 9 (a) and (d) shows that even in the presence of the extract, the steel also corroded in the medium, but there was an improvement in the metal surface morphology. This improvement indicates that the inhibitor molecules have adsorbed on the active sites parallel to the electrode surface, increasing the surface coverage of the metal, consequently, the area exposed to the corrosive medium has decreased [27-30].

These images are in agreement with the electrochemical and gravimetric results in which a total coverage of the steel surface was observed by the molecules of the adsorbed cocoa shell powder of 58.5%. In contrast, for the hydroalcoholic extract, the metal surface total coverage by the adsorbed inhibitor molecules was 76.6%, thus demonstrating a higher surface coverage and, consequently, a better protection against corrosion.

4. CONCLUSIONS

The analysis of the results indicates that the hydroalcoholic extract, obtained from the cocoa bean shell, provides better protection to the corrosion of the metallic surface in NaCl when compared to the cocoa shell in its powder form.

For both forms of inhibitor evaluated, the electrochemical impedance results showed that with the increase of the inhibitor concentration, lower corrosion efficiency inhibition values were obtained. These results were confirmed by gravimetric tests, demonstrating maximum corrosion inhibition efficiency for the lowest concentration of inhibitor studied (0.44 g.L^{-1}), whose values were equivalent to 58.48% for the cocoa shell powder and 76.61% for the extract.

However, according to EIS results, there was a decrease in inhibition efficiency with immersion time, indicating that both products studied should not be used for long immersion periods.

The FTIR spectra of the cocoa shell powder and extract showed some functional groups that can be attributed to the presence of cellulose, hemicellulose, lignin, fatty acids, flavonoids and alkaloids (theobromine and caffeine) capable of promoting adsorption on the steel surface, minimizing the corrosive process. The optical images confirmed a better protection of the metallic surface in the presence of the extract when compared to the cocoa shell powder.

Finally, for all the concentrations studied, the cocoa shell powder did not represent an efficient inhibitor, but for the concentration of 0.44 g.L^{-1} of hydroalcoholic extract, a good performance was verified as a corrosion inhibitor of SAE 1008 carbon steel in 0.5 mol.L^{-1} sodium chloride solution.

5. ACKNOWLEDGEMENTS

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