

**Evaluation of Efficiency of avocado seed powder (*Persea Americana*) as a corrosion inhibitor in SAE 1008 carbon steel in acidic medium****Avaliação da eficiência da semente de abacate em pó (*Persea Americana*) como inibidor de corrosão em aço carbono SAE 1008 em meio ácido**

DOI:10.34117/bjdv6n10-227

Recebimento dos originais: 08/09/2020

Aceitação para publicação: 09/10/2020

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**ABSTRACT**

Having in mind that the synthetic inhibitors, currently used to prevent corrosion are aggressive to the environment, natural inhibitors, might be a valid alternative and an innovative solution to this problem, due to its low cost, sustainability and its eco-friendly profile. In this work, a study was carried out on the evaluation of efficiency of avocado seed powder (*Persea Americana*) as inhibitor on the corrosion of SAE 1008 carbon steel in acidic medium (HCl 0.5 mol.L<sup>-1</sup>). The avocado seed powder was obtained from milling and sieving at 170 mesh. Different concentrations (0.44 g L<sup>-1</sup>; 0.77 g L<sup>-1</sup>; 1.11 g L<sup>-1</sup>; 1.44 g L<sup>-1</sup>; 1.77 g L<sup>-1</sup>) of avocado seed powder were added in HCl solution. The efficiency of the inhibitor was measured by electrochemical techniques, such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves, as well as gravimetric tests. The chemical characterization of the inhibitor was performed by Fourier transform infrared spectroscopy (FTIR), while the morphological characterization was obtained by optical microscopy. The FTIR characterization reveals the presence of compounds formed by heteroatoms such as nitrogen and oxygen in functional groups known to prevent the corrosion process. The results provided by these tests showed that the tendency of this inhibitor is to increase the corrosion resistance as the concentration of the inhibitor also increases, revealing that the inhibitor is a promising alternative when it comes to avoiding corrosive processes on the surface of the SAE 1008 carbon steel.

**Keywords:** Green inhibitor; Carbon steel; Acidic medium; Avocado seed; EIS.

**RESUMO**

Tendo em mente que os inibidores sintéticos, atualmente utilizados para prevenir a corrosão são agressivos ao meio ambiente, os inibidores naturais podem ser uma alternativa válida e uma solução inovadora para este problema, devido a seu baixo custo, sustentabilidade e seu perfil ecologicamente correto. Neste trabalho, foi realizado um estudo sobre a avaliação da eficiência da semente de abacate em pó (*Persea Americana*) como inibidor da corrosão do aço carbono SAE 1008 em meio ácido (HCl 0,5 mol.L<sup>-1</sup>). O pó de semente de abacate foi obtido da moagem e peneiração a 170 mesh. Diferentes concentrações (0,44 g L<sup>-1</sup>; 0,77 g L<sup>-1</sup>; 1,11 g L<sup>-1</sup>; 1,44 g L<sup>-1</sup>; 1,77 g L<sup>-1</sup>) de pó de semente de abacate foram adicionadas em solução de HCl. A eficiência do inibidor foi medida por técnicas eletroquímicas, tais como a espectroscopia de impedância eletroquímica (EIS) e curvas de polarização potenciodinâmicas, bem como testes gravimétricos. A caracterização química do inibidor foi realizada pela espectroscopia de infravermelho de transformada de Fourier (FTIR), enquanto a caracterização morfológica foi obtida por microscopia óptica. A caracterização FTIR revela a presença de compostos formados por heteroátomos, como nitrogênio e oxigênio, em grupos funcionais conhecidos para evitar o processo de corrosão. Os resultados fornecidos por estes testes mostraram que a tendência deste inibidor é de aumentar a resistência à corrosão à medida que a concentração do inibidor também aumenta, revelando que o inibidor é uma alternativa promissora quando se trata de evitar processos corrosivos na superfície do aço carbono SAE 1008.

**Palavras-chave:** Inibidor verde; Aço carbono; Meio ácido; Semente de abacate; EIS.

**1 INTRODUCTION**

The avocado (*Persea Americana*), commonly used for culinary purposes and in the cosmetics industry has had, for thousands of years, great importance in the diet and in the culture of many countries<sup>1,2</sup>. Archeological evidence in Mexico shows that its consumption can be traced back nearly 10000 years<sup>2</sup>. With the colonization process of the Americas, as well the African continent, this fruit

was spread throughout the tropics and sub tropics<sup>3</sup>. Nowadays, it can be found practically all around the world.

According to the Major Tropical Fruits - Preliminary Market Results for 2019, provided by the Food and Agriculture Organization of the United Nations (FAO), the avocado was expected to reach 29% of the total world trade in major tropical fruits, coming only behind the pineapple (46%)<sup>4</sup>. In Brazil, the avocado is mainly produced in the south and southeastern regions and its production caters mostly to the domestic market<sup>8</sup>. Nevertheless, South America was expected to contribute with 564,532 tonnes of avocado world gross export, and 9000 tonnes of that value corresponds to Brazil only, making the country one of the greatest exporters of avocado in South America.

Being known as the “poor man’s butter”, the avocado is a fruit with high nutritional value, rich in water, dietary fiber, monounsaturated fatty acids, vitamins, minerals and phytochemicals such as lutein, phenolic antioxidants, and phytosterols<sup>10</sup>. Which is why this fruit is usually associated with human health research. Despite of the many advantages of the consumption and use of the fruit, commonly, it’s not given any purpose, by the industry or the consumers, to the peel or to the seed. Therefore, those residues are generally discarded.

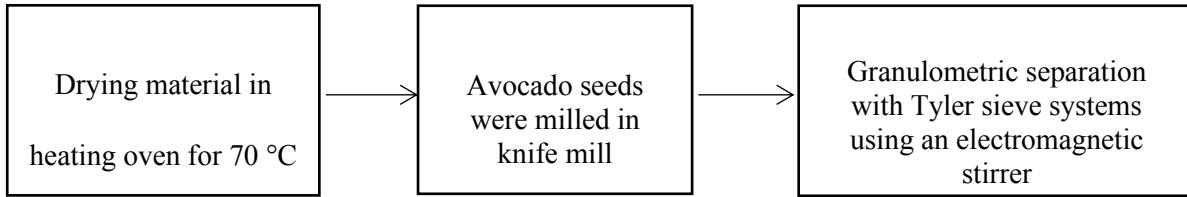
It’s well established that vegetable tissues, in general, have in their composition phytochemicals such as tannins, polyphenols, flavonoids, phlorotannins, anthraquinones, saponins, alkaloids, organic sugars, and others<sup>12</sup>. Each one of these phytochemicals can interact with metallic surfaces and inhibit corrosive mechanisms of anodic, cathodic (or both) nature<sup>12, 15</sup>. This makes the use of inhibitors extracted from vegetable sources a promising field of study.

Repurposing production waste is a way to add value to the production chain. This means that whenever it’s possible, the residues of a process should be the raw material to another process. Avocado seed is a sustainable, ecofriendly, non-toxic, ecologically sound, considerably available product from renewable sources. Hence, this residue is an interesting possibility for a corrosion prevention study<sup>12, 14, 15, 16</sup>.

## **2 EXPERIMENTAL PROCEDURE**

To begin the experiments, first, it is necessary to obtain the inhibitor from the avocado seed powder. After washing, and cutting the avocados seeds, they were submitted to the process described in Flowchart 1.

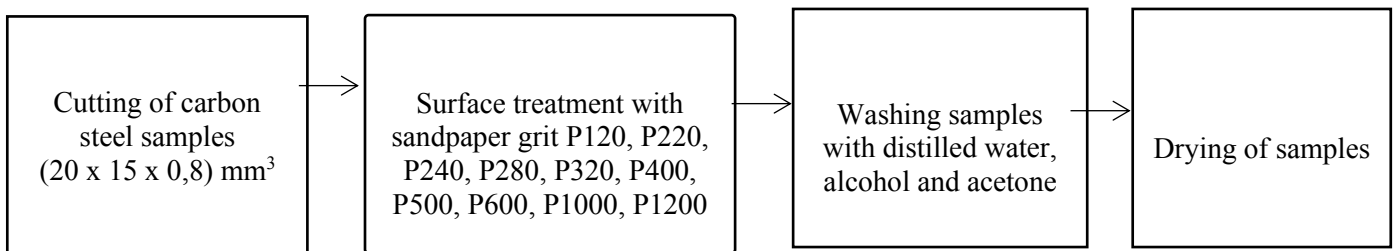
Flowchart 1 - Process of obtaining avocado seed powder.



The 170 mesh granulometry size was selected as the avocado seed powder, and further on, tested as a corrosion inhibitor. Once the avocado seed powder is obtained, it is necessary to prepare the steel for the upcoming tests, which means to clean the steel's surface, aiming to remove any impurities or corrosion products<sup>11</sup>. This process is shown below, in Flowchart 2.

The resistance to corrosion was tested with SAE (Society of Automotive Engineers) 1008 carbon steel. Due to the carbon content (0.08%), this steel has good performance in forming, and has good ductility. Other elements, such as Fe (99.31-99.7 %), Mn (0.30-0.50%), P (0.040%), and S (0.050%) are usually also present in this steel composition<sup>13</sup>.

Flowchart 2 - Surface treatment performed on SAE 1008 carbon steel samples.



The corrosion resistance was measured, in triplicate with a Metrohm Autolab model PGSTAT302N potentiostat / galvanostat, with impedance module, controlled by NOVA 1.11 software. For data processing, was used the Microcal® Origin® 8.0 software. The electrochemical cell is constituted of three electrodes: Ag | AgCl | KCl sat as reference electrode, a rhodium-coated titanium wire counter electrode and a working electrode (SAE 1008 carbon steel) with an exposed area of 1 cm<sup>2</sup>. The electrolyte was an aqueous solution of HCl 0.5 mol.L<sup>-1</sup> in the absence and in the presence of different avocado seed powder concentrations: 0.44 g L<sup>-1</sup>, 0.77 g L<sup>-1</sup>, 1.11 g L<sup>-1</sup>, 1.44 g L<sup>-1</sup> and 1.77 g L<sup>-1</sup>. These concentrations were used by the group in natural inhibitor studies and were maintained for means of comparison<sup>18,19,34</sup>.

Initially, the open circuit potential (OCP) was measured for 90 min, for the stabilization of the corrosion potential. The electrochemical impedance spectroscopy (EIS) tests were carried out in the OCP in the frequency range from 100 kHz to 10 mHz with 10 points per decade and a 10 mV perturbation amplitude (rms). For quantitative analysis, the EIS data were processed with Z-View software. The anodic (-30 mV vs OCP to + 250 mV vs OCP) and cathodic (+ 30 mV vs OCP to -

250 mV vs OCP) curves were obtained with separate working electrodes, both with sweep rate of  $0.5 \text{ mV s}^{-1}$ .

The chemical characterization of the avocado seed powder was executed by Fourier Transform Infrared Spectroscopy (FTIR) using the Attenuated Total Reflectance (ATR) Thermo Scientific Nicolet, model IS10. The spectrum was obtained in the average wavelength range from  $4000$  to  $650 \text{ cm}^{-1}$ , with a resolution of  $4 \text{ cm}^{-1}$ .

The gravimetric (weight loss) tests were carried through in triplicate and followed the procedure established in the technical standard ASTM G1<sup>\*\*</sup>. The carbon steel samples, previously sanded and cleaned, were weighted in an analytical scale (Marte, model AY220) with  $0,1 \text{ mg}$  of precision, and then immersed in a HCl solution  $0.5 \text{ mol.L}^{-1}$  in the absence and in the presence of the five inhibitor concentrations previously mentioned. The samples remained immersed for  $120 \text{ min}$ . After this time, the samples were removed from immersion, brushed with a soft brush, washed with distilled water, alcohol, acetone, and finally dried with a heat gun, being posteriorly weighted to verify the weight loss. The performed tests were made in a non-agitated, aerated solution.

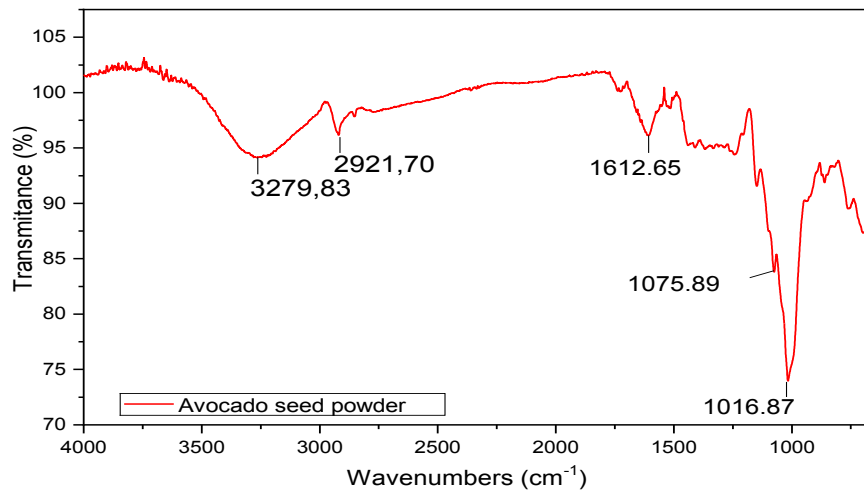
The surface morphology of the samples after immersion in HCl solution  $0.5 \text{ mol.L}^{-1}$  with and without the inhibitor was analyzed by the optical microscope Labomed CZM6, after  $120 \text{ min}$  of immersion.

### 3 RESULTS

#### 3.1 CHEMICAL CHARACTERIZATION (FTIR)

The infrared spectrum, observed in Figure 1, was obtained from the avocado seed powder. The peak centered at  $3279 \text{ cm}^{-1}$  can be attributed to O-H and also N-H groups, which can be found in water or amines<sup>9,18</sup>. The peak at  $2921 \text{ cm}^{-1}$  can be associated to C-H stretching present in organic compounds. Around  $1710 \text{ cm}^{-1}$  is noticeable a band that can be associated to the carboxylate group (C=O), usually found in flavonoids and fatty acids. The band present in the  $1150 \text{ cm}^{-1}$  refers to aromatic rings, while the bands covered by the  $1060\text{-}1080 \text{ cm}^{-1}$  and  $1010\text{-}1040 \text{ cm}^{-1}$  ranges are referring to the stretching vibration of the C-O bond of alcohols and phenols<sup>15,18,28,34</sup>.

Figure 1 – FTIR spectra of avocado seed powder.



With resembling results, Lara-Valencia *et al.*(2018) concluded that the material obtained from the avocado seed is rich in polysaccharides since there is evidence of the presence of its functional groups, furthermore it contains small amounts of tannins, among other compounds.

Therefore, it can be said that the natural inhibitor derived from the avocado seed probably contains oxygen and nitrogen atoms in functional groups and aromatic rings, which are generally found in the structure of other corrosion inhibitors, being attributed to those compounds, the inhibitory properties.<sup>12, 15, 18</sup>

### 3.2 GRAVIMETRIC TESTS

The results displayed in Table 1, were calculated based on the data acquired from the weight loss test. The, corrosion rate for the SAE 1008 carbon steel, in the presence and absence of the avocado seed powder was quantified using Equation 01, in which  $C_R$  represents the corrosion rate value,  $\Delta W$  the average weight loss in grams,  $A$  is the total exposed area and  $t$  is the immersion time in hours<sup>27</sup>.

$$C_R = \frac{\Delta W}{A.t} \quad (01)$$

Using the previous value found with Equation 01, the Faraday's constant corresponding to 96500 and  $E_{q_{metal}}$  (gram equivalent for carbon steel, which was assumed to be 27.93 g, corresponding to pure iron<sup>18,34</sup>) is possible to calculate the corrosion current density by Equation 02.

$$i_{corr} = C_R \frac{96500}{Eq_{metal}} \quad (02)$$

The inhibition ( $\eta_{WL}$ ) was calculated by Equation 03, where  $C_{R0}$  and  $C_{Ri}$  are the carbon steel corrosion rates in the absence and presence of inhibitor, respectively.

$$\eta_{WL} = \left(1 - \frac{C_{Ri}}{C_{R0}}\right) \times 100 \quad (03)$$

**Table 1-** Corrosion rate ( $C_r$ ), corrosion current density ( $i_{corr}$ ), degree of coverage of the metallic surface ( $\theta$ ) and inhibitory efficiency ( $\eta_{WL}$ ) obtained by the gravimetric analysis of SAE 1008 carbon steel after 120 min immersion in HCl solution 0.5 mol.L<sup>-1</sup> in the absence (blank) and in the presence inhibitors for different concentrations.

Concentration of inhibitor (g L <sup>-1</sup> )	$C_r$ ( $\mu\text{A}/\text{cm}^2$ )	$i_{corr}$ (A.cm <sup>2</sup> )	$\theta$	$\eta_{WL}$ (%)
<b>Blank</b>	1.06E-05	-	-	-
<b>0.44</b>	3.34E-06	0.0115	0.68	68
<b>0.77</b>	1.81E-06	0.0062	0.83	83
<b>1.11</b>	1.71E-06	0.0059	0.84	84
<b>1.44</b>	1.32E-06	0.0046	0.88	88
<b>1.77</b>	8.48E-07	0.0029	0.92	92

The results presented in Table 1, show that the powder's efficiency increased up to 92% when 1.77 g L<sup>-1</sup> was added to the electrolyte solution. It's noticed that the inhibitor demonstrated a performance above 70% in almost all concentrations, which, according to the classical literature, is an indicative of a efficient inhibitor<sup>30</sup>.

It's observed also, that increasing the inhibitor's concentration, not only the efficiency against the corrosion process is increased, but corrosion rate and the corrosion current density are lowered. According to the literature, this occurs because of the absorption of inhibitory molecules on the metal surface, which prevents the electron transference between the metallic surface and the electrolyte<sup>18, 34, 35</sup>. The capacity of an inhibitor to perform as described is intimately connected to the chemical structure of its compounds and its physicochemical properties. It can be said then, that the decrease in the mass loss is associated to the adsorption of the inhibitor to the metallic surface<sup>12, 15, 27</sup>.

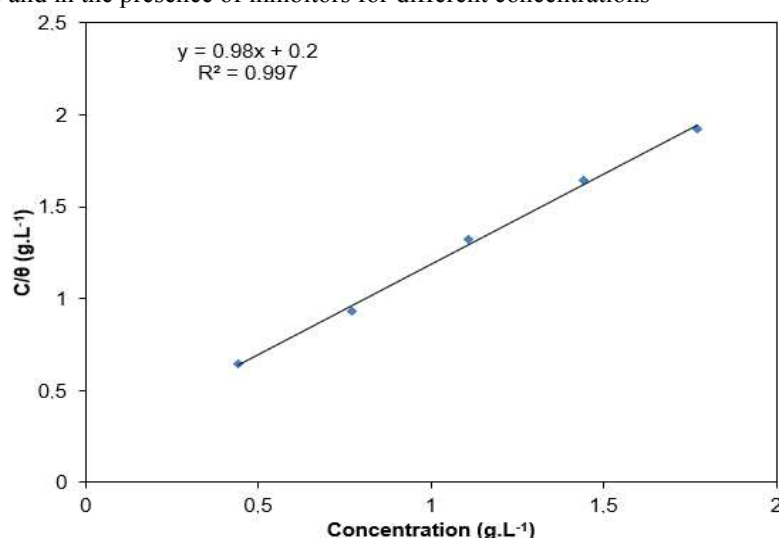
### 3.3 ADSORPTION ISOTHERM

According to literature, the mechanism of inhibitors on metal surface is explained by adsorption process. Information about the interaction between inhibitors molecules and substrate

surface are obtained by adsorption isotherm<sup>21</sup>. The Freundlich, Frumkin, Temkin and Langmuir adsorption isotherms are commonly tested to verify the inhibitor mechanism; however, the Langmuir is the most found in corrosion inhibitors, in this case, it was the first to be studied<sup>18, 21</sup>. Langmuir isotherms lines for SAE 1008 carbon steel, after 120 min immersion in HCl solution 0.5 mol.L<sup>-1</sup> in the absence (blank) and in the presence of inhibitors for different concentrations, are presented in Figure 2.

The isotherms lines observed in Figure 2 indicate adsorption of an inhibitor monolayer in subtract surface. The linear correlation coefficient ( $R^2$ ) above 0,99 indicate that adsorption follows Langmuir isotherm ( $R^2=0,997$ ), in this case, the adsorption products occupy places on carbon steel surface. This behavior agrees with other studies for natural inhibitors.<sup>18,19,20</sup>

**Figure 2-** Isotherms Langmuir Lines for SAE 1008 carbon steel after 120 min immersion in HCl solution 0.5 mol.L<sup>-1</sup> in the absence (blank) and in the presence of inhibitors for different concentrations



The adsorption standard Gibbs free energy values ( $\Delta G^{\circ}_{ads}$ ) were calculated by the Equation 4 to acquire information about the type of adsorption:

$$\Delta G^{\circ}_{ads} = -RT \ln (C_{H_2O} K_{ads}) \quad (04)$$

Where  $R$  is the universal gas constant (8.3147 J.mol<sup>-1</sup>.K<sup>-1</sup>),  $T$  means the absolute temperature (298 K),  $C_{H_2O} = 1000$  g/L is the water concentration and  $K_{ads}$  is related to the adsorption constant<sup>21</sup>. The  $\Delta G^{\circ}_{ads}$  of adsorption at 25°C, obtained from Eq. 4, were -17,15 kJ.mol<sup>-1</sup>. The literature reports that negative values for  $\Delta G^{\circ}_{ads}$  indicates that the adsorption, when the inhibitors are added in the acid medium, is a spontaneous process<sup>21</sup>. Tawfik, Elaal-Abd e Aiad (2016) reports that, generally,



$\Delta G^{\circ}_{\text{ads}} \leq -20 \text{ kJ.mol}^{-1}$  is related to physical adsorption which has weak electrostatic interaction between the inhibitor molecules and metal surface, otherwise, values in the region of  $-40 \text{ kJ.mol}^{-1}$  are associated with chemical adsorption, which involves strong interaction between them with electrons charge transfer or coordination.

Thus, the  $\Delta G^{\circ}_{\text{ads}}$  values obtained for inhibitor are less negative than  $-20 \text{ kJ.mol}^{-1}$  indicating that the adsorption mechanism is controlled by the physisorption process for the inhibitors on carbon steel in the studied conditions, forming adsorbed layers with less stability on metal surface.

### 3.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

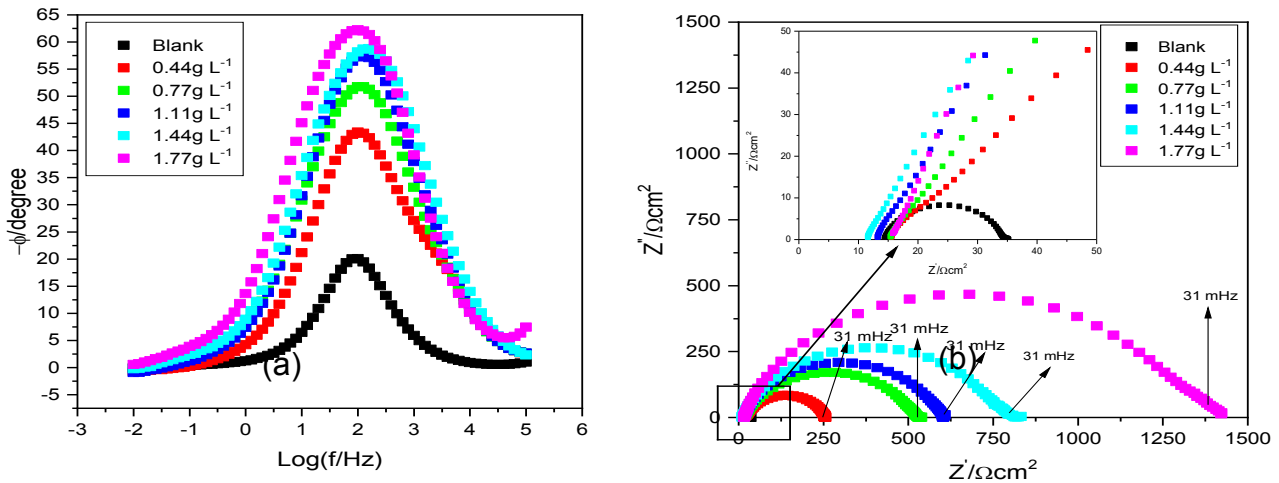
The results provided by the EIS tests are displayed in figure 3 initially; it is perceived that the shape of the diagrams is maintained when the inhibitor is added to the electrolyte, which means that the corrosion mechanism is not changed by the avocado seed powder.<sup>34</sup>

Examining the Nyquist plot (Figure 3a) is possible to notice that the capacitive arch is always larger in the presence of the avocado seed powder than in the absence of the tested inhibitor. Furthermore, it can be said that elevating the amount of the inhibitor added to the electrolyte can cause growth of the diameter and the capacitive behavior of the arch, indicating elevation of the corrosion resistance. That means that the avocado seed powder can actually promote corrosion resistance.<sup>18, 19, 43</sup>

Aligned with the Nyquist plot, the results presented by the Bode diagram on the phase angle (Figure 3b), showed that in the presence of any of the concentrations of the avocado seed powder, the phase angle, increase its value, reaching a higher phase angle value and covering a bigger frequency range. That is probably associated with a more effective adsorption of the inhibitory compounds on the metallic surface, which hinders the corrosive process.<sup>27, 34-36</sup>

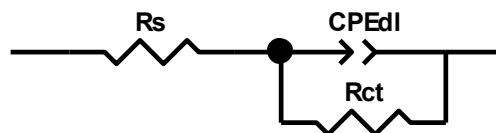
In both diagrams, is very clear that the  $1.77 \text{ g L}^{-1}$  concentration provides the highest value of impedance and phase angle, therefore being the one that presents the optimal performance in inhibiting the corrosion process.

**Figure 3-** EIS diagrams obtained for SAE 1008 carbon steel in HCl 0.5 mol.L<sup>-1</sup> in the absence and in the presence of different concentrations of avocado seed powder: (a) Nyquist, (b) Bode Phase Phase angle.



The impedance spectra (Fig. 3) were fitted to the electrical equivalent circuit (EEC) model displayed in Figure 4 Using the Z'view software. In this circuit  $R_s$  is the solution resistance,  $CPE_{dl}$  is the electric double layer capacitance and  $R_{ct}$  is the charge transference resistance. This model is frequently used to fit EIS plots of carbon steel in acidic medium, with or without inhibitor. <sup>18, 19, 25, 34-36</sup>

**Figure 4-**Equivalent electrical circuit



The CPE impedance ( $Z_{CPE}$ ) can be expressed according to equation 05<sup>19, 20</sup>:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (05)$$

In that equation:  $Y_0$  is the CPE value,  $j$  is an imaginary number (being  $j^2$  equivalent to  $-1$ ),  $\omega$  is the angular frequency and  $n$  is the dispersion factor (varies between 0 and 1, and indicates the homogeneity or rugosity of the surface). When this factor is equal to 1, it is said that the surface is homogeneous, thus being related to a pure capacitor, revealing the behavior of an ideal electrode. <sup>34,</sup>

Knowing the resistance to the charge transference ( $R_{ct}$ ) value, expressed in the equivalent circuit, it is possible to calculate the efficiency of the corrosion inhibitors ( $\eta_{WL}$ ), as is presented in the equation 06:

$$\eta_{WL} = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \quad (06)$$

$R_{ct,0}$  represents the resistance to the charge transference in the absence of the natural inhibitor,  $R_{ct}$  is the resistance to the charge transference in the presence of the natural inhibitor.

The statistical value  $\chi^2$  (chi-squared) represents the harmony between the adjusted data from the equivalent circuit and the experimental data.<sup>18, 19, 35</sup> The parameters found from the equivalent circuit are expressed in Table 2.

Table 2. Parameters found from the EEC.

Concentration of inhibitor (g L <sup>-1</sup> )	$r_s$ ( $\Omega$ cm <sup>2</sup> )	$r_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$CPE_{dl}$ ( $\mu F$ cm <sup>-2</sup> s <sup>(<math>n-1</math>)</sup> )	$N$	$\chi^2$	Inhibition in equivalent circuit (%)
Blank	14.42	19.89	$2.87 \times 10^{-4}$	0.89	$1.77 \times 10^{-4}$	-
0.44	19.69	239.9	$9.68 \times 10^{-5}$	0.76	$7.67 \times 10^{-4}$	92%
0.77	15.3	507.7	$8.13 \times 10^{-5}$	0.75	$7.31 \times 10^{-4}$	96%
1.11	13.15	583.1	$5.67 \times 10^{-5}$	0.79	$9.98 \times 10^{-4}$	97%
1.44	11.37	753.2	$5.39 \times 10^{-5}$	0.78	$2.47 \times 10^{-4}$	97%
1.77	15.6	1273	$2.39 \times 10^{-5}$	0.81	$1.61 \times 10^{-3}$	98%

From Table 2 is clear, that the  $\chi^2$  values found are all inferior to  $1.00 \times 10^{-2}$  meaning that the chosen EEC and the experimental data validate each other. The values of the dispersion factor ( $n$ ) are relatively close to 1, indicating close proximity to an ideal capacitors homogeneous surface.<sup>35</sup>

It is noticed, when observing the results from the fitting, that the  $CPE_{dl}$  values decrease, as the concentration of avocado seed powder increases, which indicates the adsorption of inhibitory molecules on the steel's surface, promoting superficial coverage increase, allowing less of the surface area to be exposed to the acidic medium<sup>27</sup>. Another aspect that deserves attention is the increase in the  $R_{ct}$  value as the amount of powder is in the solution is increased. This is related to

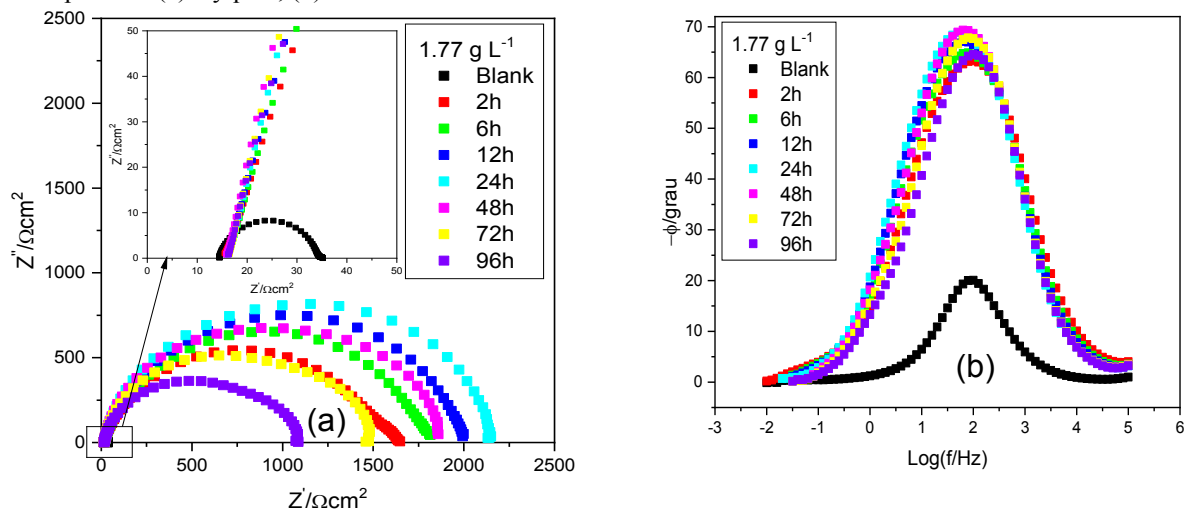
the hindered electronic exchange between the substrate and the electrolyte<sup>31</sup>. Consequently, it can be said that the absorption of molecules on the surface of the substrate can form a barrier that shelters the surface from the corrosion process.<sup>23</sup>

The highest value of efficiency was found for the concentration  $1.77 \text{ g L}^{-1}$ . Even at the lowest concentration ( $0.44 \text{ g L}^{-1}$ ), the efficiency was above 70%, which is considered by the literature to be the minimum value for an inhibitor to be judged as an efficient corrosion protection<sup>30</sup>. Hence, avocado seed powder can represent an effective corrosion inhibitor for SAE 1008 carbon steel in HCl solution  $0.5 \text{ mol.L}^{-1}$ .

#### 4.5 EVALUATION OF IMMERSION TIME IN THE CORROSION INHIBITION

Knowing that the  $1.77 \text{ g L}^{-1}$  concentration had the best performance in the gravimetric and EIS tests, this concentration was submitted to an evaluation of its efficiency over different time periods. The results are displayed in Figure 5.

**Figure 5-** EIS diagrams for SAE 1008 carbon steel in HCl  $0.5 \text{ mol.L}^{-1}$  in the presence avocado seed for different immersion periods: (a) Nyquist, (b) Bode Phase.

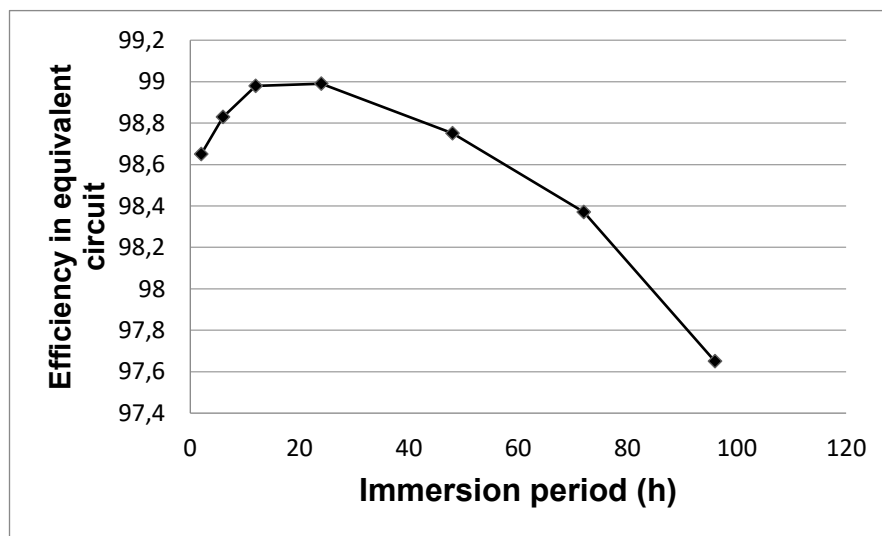


From the Figure 5a it is perceived that the impedance continues to increase only decaying in value when the sample has been immersed for more than 24h. It is known, that the forces involved in the physisorption process are weak. Hence, the decrease in the impedance value is probably related to the interaction of the adsorbed molecules.<sup>39, 40</sup>

Complementing the Nyquist plot, the phase angle, shows the existence of a barrier layer, since that the plot, for all immersion periods reaches higher values of phase angles and occur in a broader range of frequency than the sample without the presence of the avocado seed powder.<sup>19, 34</sup>

Comparable to the fitting previously tested for different concentrations, the same was tested for different immersion periods. The results also showed a  $\chi^2$  inferior to  $1.00 \times 10^{-2}$ , confirming that the equivalent circuit and the experimental data validate each other once again. In this sense, the efficiency of the inhibitor over different immersion periods was calculated according to Equation 05. The results are displayed in Figure 5.

**Figure 6** - Efficiency of the inhibitor over different immersion periods.

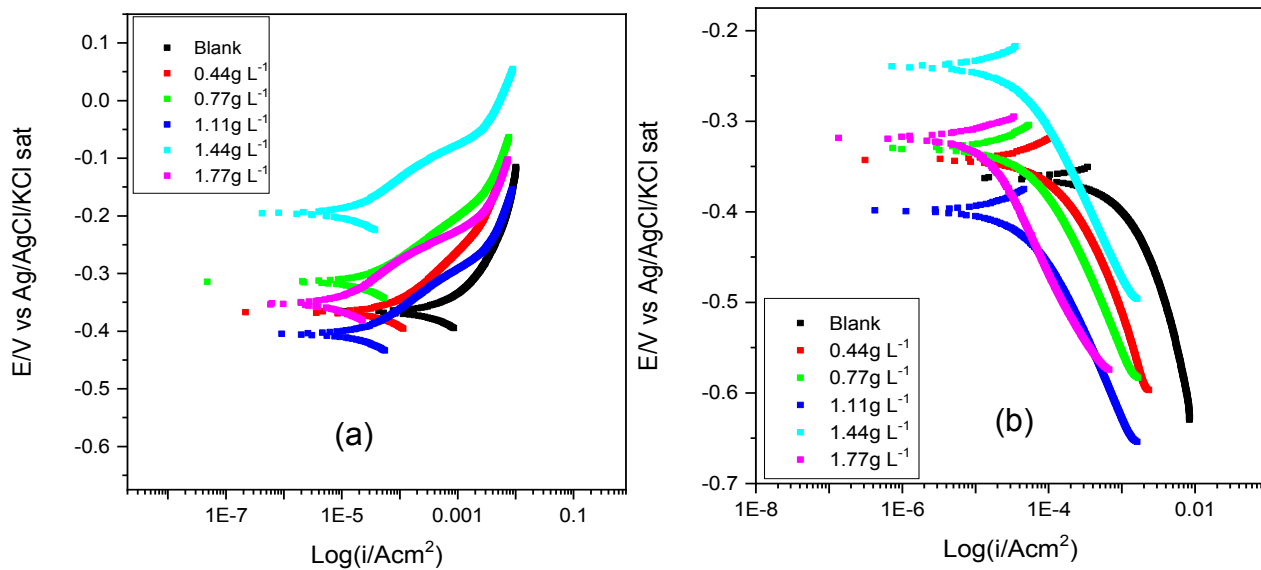


From figure 6, the highest efficiency value is achieved around 24h (98.9%), subsequently the efficiency decreases, showing that the avocado seed powder should not be applied in immersion periods longer than 24h. The decrease in the efficiency can be explained by the likely deterioration of the barrier layer, caused by the loss of the inhibitory properties of the physiologically adsorbed molecules, allowing the substrate to be in contact with the aggressive environment, letting the corrosive process to occur as expected.<sup>19, 20, 34</sup>

#### 4.6 POTENCIODYNAMIC POLARIZATION CURVES

In an attempt to determine what is the inhibitory effect of the avocado seed powder (anodic, cathodic or both), the potentiodynamic polarization curves obtained after 110 min of immersion and after OCP in HCl solution  $0.5 \text{ mol.L}^{-1}$ , in the absence and presence of the five concentrations of the inhibitor. The results are shown in Figure 7.

**Figura 7-** Anodic (a) and cathodic (b) polarization curves obtained for SAE 1008 carbon steel after 110 min of immersion in 0.5M HCl solution in the absence and in the presence of different concentrations of the tested inhibitor.

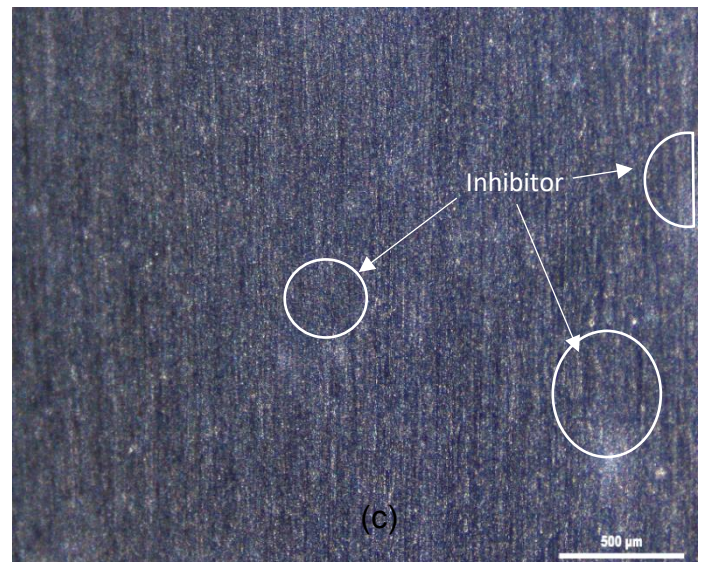
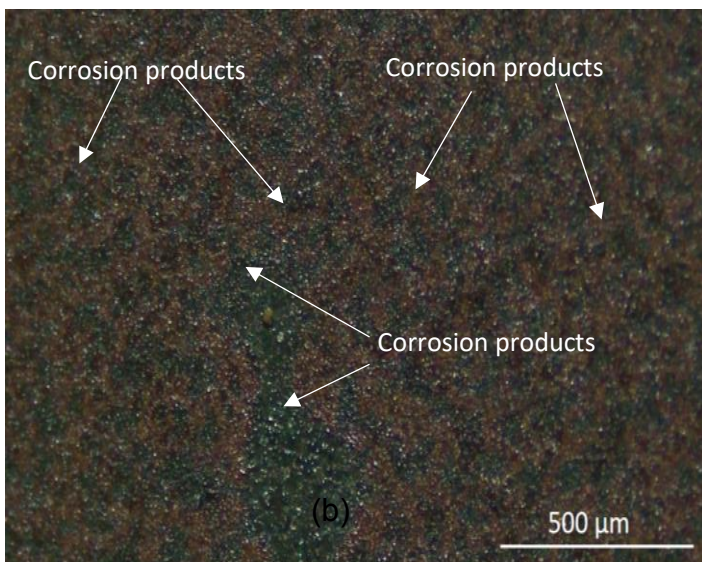
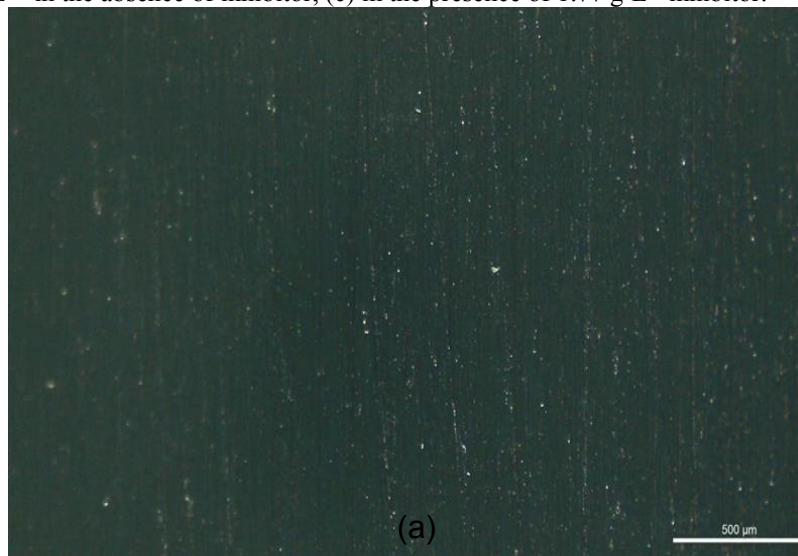


It is possible to see in the results, that the corrosion current density values are lower for the samples in the presence of avocado seed powder, and higher for the sample in the absence of the tested inhibitor for all five tested concentrations, in both anodic and cathodic polarization curves. With this information it can be said that the inhibitor act as a mixed (both anodic and cathodic) inhibitor. <sup>12, 19, 29, 44</sup>

#### 4.7 SURFACE MORFOLOGY

After the gravimetric tests, the samples were analyzed in an optical microscope. The images obtained are for the sample before immersion, after immersion in a HCl solution 0.5 mol.L<sup>-1</sup> without the inhibitor and with the concentration that provided the best efficiency in the previous tests (1.77 g L<sup>-1</sup>). The images are exposed in Figure 8.

**Figure 8-** Images for SAE 1008 Carbon Steel surface (500  $\mu\text{m}$ ): (a) before immersion, (b) after immersion for 120min in  $\text{HCl } 0.5 \text{ mol.L}^{-1}$  in the absence of inhibitor, (c) in the presence of  $1.77 \text{ g L}^{-1}$  inhibitor.



In Figure 8a is shown the image of a surface free of corrosion products, with only a few minor scratches due to the sample's preparation process (Flowchart 2). Nevertheless, the surface in figure 8b, which corresponds to the surface after 120 min of immersion in  $\text{HCl } 0.5 \text{ mol.L}^{-1}$  in the absence of the tested inhibitor, is entirely covered in corrosion products, as highlighted in the image. In contrast, Figure 8c, shows a surface with little corrosion products on the sample's surface even after 120 min of immersion. The few spots, accentuated in Figure 8c, can be associated with the avocado seed powder's presence on the solution.

Similarly, R. Saratha, S. V. Priya, P. Thilagavathy (2009) also investigated with an optical microscope the effects of the *citrus aurantiifolia* leaves (abbreviated to CAL) extract as corrosion inhibitor for mild steel in  $\text{HCl } 1 \text{ mol.L}^{-1}$ . After 168h period of exposition, they found that the

samples that were exposed to aggressive environment in the presence of the natural inhibitor, with an efficiency of 97.5%, showed relative superficial improvement in comparison to the sample exposed to the solution in the absence of the CAL.

In this sense, it can be stated that the inhibitory molecules found in the avocado seed powder had a satisfactory adsorption and created a reasonably homogenous protective film, since there is little to no corrosion products in the substrate surface. That improved the visual aspect of the steel's surface, while also inhibiting the corrosion process, helping to confirm the experimental data found on the previous tests.

#### 4 CONCLUSION

The results showed that the avocado seed powder is a potential corrosion inhibitor for SAE 1008 Carbon Steel in HCl 0.5 mol.L<sup>-1</sup>, with an efficiency of 92% in the gravimetric test for the 1.77 g L<sup>-1</sup> concentration. The FTIR spectrum provided results that demonstrate that the tested inhibitor has components usually found in natural inhibitors, formed by heteroatoms such as Nitrogen and Oxygen (C=O, N-H, C-H, O-H, C-O), as well as aromatic rings, that could be adsorbed in to the metallic surface, building a barrier that shields the substrate from the corrosion process.

The adsorption isotherm showed that the process follows the Langmuir isotherm, which means that the molecules are probably adsorbed physically. The potentiodynamic polarization curves showed that the inhibitor not only can decrease the corrosion current densities, hindering the corrosion process, but can also act as a mixed inhibitor, affecting both anodic and cathodic reactions.

Contributing to these results, the EIS data showed an increase in the impedance value and, for the Bode Phase, higher values of phase angle, and wider coverage of frequency range, in all of the five tested concentrations. Showing that the tested powder provided stronger corrosion resistance, while also forming a barrier that protected the electrode from the aggressive environment, confirming what was expected, given the FTIR results. Correspondingly, the fitting results to the chosen electrical equivalent circuit provided an efficiency of 98% to the 1.77 g L<sup>-1</sup> concentration, which seemed suitable to the weight loss test results, as well the images obtained from the optical microscope.

Therefore, the avocado seed powder is a promising inhibitor and shows potential to future applications.



## ACKNOWLEDGEMENT

Authors would like to acknowledge to FAPESB [Amparo Foundation for Research of the State of Bahia (BOL0047/2016)] for financial support, the BIOMA (Environment and Bioenergy Group) of State University of Santa Cruz (BA, BR) for FTIR analysis, LAMMA (Environment and Materials Laboratory) of State University of Santa Cruz (BA, BR) for support, and CME (Electronic Microscopy Center) of State University of Santa Cruz (BA, BR) for Optical images.

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