Evaluation of vegetables residues as corrosion inhibitors

Avaliação de resíduos de vegetais como inibidores de corrosão

Evaluación de residuos de verduras como inhibidores de corrosión

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Abstract
This work investigates the use of (Allium sativum L.) garlic peel extract, and (Theobroma L) cacao peel, as well as their synergy as a corrosion inhibitor for carbon steel in 0.5 mol.L^{-1} hydrochloric acid solution. The comparative study was performed in 1.11 g.L^{-1} of extract. The investigation was carried out using Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), gravimetric techniques and scanning electron microscopy (SEM) as chemical, electrochemical and morphological characterization techniques, respectively. Gravimetric tests results showed a reduction in the corrosion rate of the extracts, with 90.7% efficiency for garlic extract and 89% for cacao extract, however, the mixture of the compounds presented an inhibition superior to 98%, showing the great synergism between the studied species. While the EIS results showed a higher impedance module value for cacao extract compared to garlic extract. Chemical analysis for extracts of garlic and cacao obtained by FTIR showed the presence of compounds based on sulfur and nitrogen, which are responsible for corrosion inhibiting effect. The SEM images obtained showed the formation of a film which reduces the evaluation of the corrosive process. Then, it is possible to conclude, that the carbon steel surface immersed in 0.5 mol.L^{-1} HCl solution with garlic peel extracts or cacao peel extracts or both, presents a corrosion inhibiting effect.
Keywords: Corrosion inhibitors; Natural inhibitors; Allium sativum L.; Theobroma L.

Resumo
Este trabalho investiga a utilização do extrato da casca do alho (Allium sativum L.) e casca do cacau (Theobroma L.), bem como sua sinergia como inibidor de corrosão para aço carbono em solução de ácido clorídrico 0,5 mol.L^{-1}. O estudo comparativo foi realizado em 1,11 g.L^{-1} do extrato. A investigação foi realizada utilizando espectroscopia no infravermelho por transformada de Fourier (FTIR), espectroscopia de impedância eletroquímica (EIE), técnicas gravimétricas e microscopia eletrônica de varredura (MEV) como técnicas de caracterização química, eletroquímica e morfológica, respectivamente. Os resultados dos testes gravimétricos mostraram redução na taxa de corrosão dos extratos, com eficiência de 90,7% para o extrato do alho e 89% para o extrato do cacau, porém, a mistura dos compostos apresentou uma inibição superior a 98%, evidenciando o grande sinergismo entre as espécies estudadas. Enquanto os resultados do EIE mostraram um valor de módulo de impedância mais alto para o extrato do cacau em comparação com o extrato do alho. Análises químicas para extratos do alho e cacau obtidos por FTIR mostraram a presença de compostos à base de enxofre e nitrogênio, os quais são responsáveis pelo efeito inibidor da corrosão. As imagens de MEV obtidas mostraram a formação de um filme que reduz a avaliação do processo corrosivo. Conclui-se

então que a superfície do aço carbono imersa em solução de HCl 0,5 mol.L^{-1} com extrato do alho ou extrato do cacau ou ambos apresentam efeito inibidor de corrosão.
Palavras-chave: Inibidores de corrosão; Inibidores naturais; Allium sativum L.; Theobroma L.

Resumen
Este trabajo investiga el uso de extracto de cáscara de ajo (Allium sativum L.) y cáscara de cacao (Theobroma L.), así como su sinergia como inhibidor de corrosión para acero al carbono en solución de ácido clorhídrico 0,5 mol.L^{-1}. El estudio comparativo se realizó en 1,11 g.L^{-1} de extracto. La investigación se llevó a cabo utilizando espectroscopía infrarroja por transformada de Fourier (FTIR), espectroscopía de impedancia electroquímica (EIE), técnicas gravimétricas y microscopía electrónica de barrido (MEB) como técnicas de caracterización química, electroquímica y morfológica, respectivamente. Los resultados de las pruebas gravimétricas mostraron una reducción en la tasa de corrosión de los extractos, con 90,7% de eficiencia para el extracto de ajo y 89% para el extracto de cacao, sin embargo, la mezcla de los compuestos presentó una inhibición superior al 98%, mostrando el gran sinergismo entre los estudiados. especies. Mientras que los resultados de EIE mostraron un valor de módulo de impedancia más alto para el extracto de cacao en comparación con el extracto de ajo. El análisis químico de los extractos de ajo y cacao obtenidos por FTIR mostró la presencia de compuestos a base de azufre y nitrógeno, que son los responsables del efecto inhibidor de la corrosión. Las imágenes MEB obtenidas mostraron la formación de una película que reduce la evaluación del proceso corrosivo. Entonces, es posible concluir, que la superficie de acero al carbono sumergida en solución 0.5 mol.L^{-1} de HCl con extractos de ajo o extractos de cacao o ambos, presentam un efecto inhibidor de la corrosión.
Palabras clave: Inhibidores de corrosion; Inhibidores naturales; Allium sativum L.; Theobroma L.

1. Introduction

Since the human started using metallic materials, the concern about the corrosion has become a significant aspect. It has been studied in scientific circles for over 150 years, focusing on a relevant phenomenon that affects the chemical, petrochemical, construction, automotive, aerospace and white industries and communications sectors, among others, causing environmental and economic impacts (Callister, 2002).

Corrosion inhibitors can be defined as those chemical substance that when present in the corrosion system at a suitable concentration decreases the corrosion rate, without significantly changing the concentration of any corrosive agent. It is generally effective in small concentrations (Monticelli, 2017)

The corrosion inhibitors commonly used are chemicals synthetic compound (or substance) that are characterized by high costs, toxicity and harmfully to human health (Edoziuno *et al.*, 2020). Nowadays, the study of natural corrosion inhibitors becomes prominent due to be non-toxic, it has a low environment impact, it is produced from raw materials readily available and it has a low cost. In this context, the use of vegetable residue as corrosion inhibitors would be financially and environmentally advantageous, because it would reduce the number of chemicals used, ensuring better conditions of handling and disposal of such compounds. Some of the vegetable residues exhibit wide variety of chemical compounds that can act as natural inhibitors of corrosion (Marzorati, Verotta & Trasatti, 2018).

The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic middle has been reported by some research groups (Ayeni *et al.,* 2014; Onukwuli & Omotioma, 2016; Onukwuli *et al.,* 2017; Okafor, Anadebe & Onukwuli, 2019; Anadebe *et al.,* 2018*;* Gomes, 1999). Efforts to find natural organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified in the world.

Researchers have reported promising results with extract obtained from peel garlic (Barreto *et al.*,2017), cacao (Barreto *et al.,* 2018), palm biodiesel (Jakeria, Fazal & haseeb, 2015), oil cake (Santos *et al.*,2020), extract of Artemisia pallens (Garai *et al.*,2012) for different metals and media. The good performance of these natural inhibitors has been ascribed to the presence of organic functionalities such as tannins, alkaloids, nitrogen base, carbohydrates and proteins with antioxidant properties (Fadel *et al.*,2013).

Taking into consideration the interest of preserving the carbon steel, this paper has focused on evaluating the behavior of corrosion natural inhibitors of the garlic and cacao peels as well as their synergy, in the corrosion process of ASTM 1020 carbon steel in acid middle. This innovation is the main contribution of this work, considering that is a vast literature on corrosion inhibitors acting alone or in association with synthetic inhibitors, but there are few studies that investigate the performance of inhibitors together and how this relationship enhances the effects inhibitory.

2. Methodology

In this study, the ASTM 1020 carbon steel was used for the investigation of natural corrosion inhibitors effect. The surfaces of samples were prepared by grinding and degreased with distilled water, ethanol and acetone. The electrolyte was an aqueous solution of HCl 0.5 mol.$L^{-1.}$ The vegetable residues as corrosion inhibitors tested were: extract of the peel garlic *(*Allium sativum L.*)* and the peel cacao (Cacao Theobroma L*)*. The extract was obtained as follows: the powder of peel was immersed in ethanol and it was stored at room temperature for 48 h, which was filtered and placed in a rotary evaporator at 79 ºC to remove the solvent, thus obtaining the extract.

To verify the corrosion inhibitors studied and the synergism between the inhibitors were made using the concentration that showed the best performance of each inhibitor (1.11 g.L^{-1}). Table 1 presents the synergism concentration studied.

Table 1 - Synergism studies of garlic and cacao peel extract.

Synergism sample	Garlic peel extract (g.L^{-1})	Cacao peel extract	Solution Concentration g.L^{-1}
Blank	-	-	-
S1	0.78	-	0.78
S2	-	0.78	0.78
S3	1.11	-	1.11
S4	-	1.11	1.11
S5	0.33	0.78	1.11
S6	0.56	0.56	1.11
S7	0.78	0.33	1.11
S8	1.11	1.11	2.22

Source: Authors.

The corrosion resistances of the samples in the presence and absence of the corrosion inhibitors were evaluated by electrochemical impedance spectroscopy (EIS) after open circuit potential stabilization for 90 min, in a solution of HCl 0.5 mol.L^{-1}. The EIS measurements carried out in triplicate, using an electrochemical cell with three electrodes, the sample as work electrode with an exposed surface area of 1 cm², a counter electrode of titanium wire with 1.6 mm of diameter and 10 cm of high coated with rhodium, and Ag/AgCl|KCl_{Sat} as a reference electrode. The EIS data were obtained in a frequency range of 100 kHz to 10mHz in a potentiostat/galvanostats Methrom AUTOLAB using the software NOVA 10.0.

The polarization curves - ± 250 mV vs OCP potential range- were obtained from potentiostat/galvanostat Methrom AUTOLAB using the software NOVA 10.0 and the electrochemical cell with three electrodes. The efficiency of corrosion inhibitors was evaluated by gravimetric tests according to standard ASTM-G1, using rectangular electrodes (50 x 20 x 0.8) mm, with 2 h of immersion time. The polarization curves and gravimetric tests were carried out in triplicate.

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Micrographs of the electrodes surface were taken after 90 min immersion in the test electrolyte (EIS experiments) or 120 min (weight loss measurements) with and without the inhibitors using a scanning electron microscope (SEM) Quanta 250F after weight loss measurements and EIS experiments.

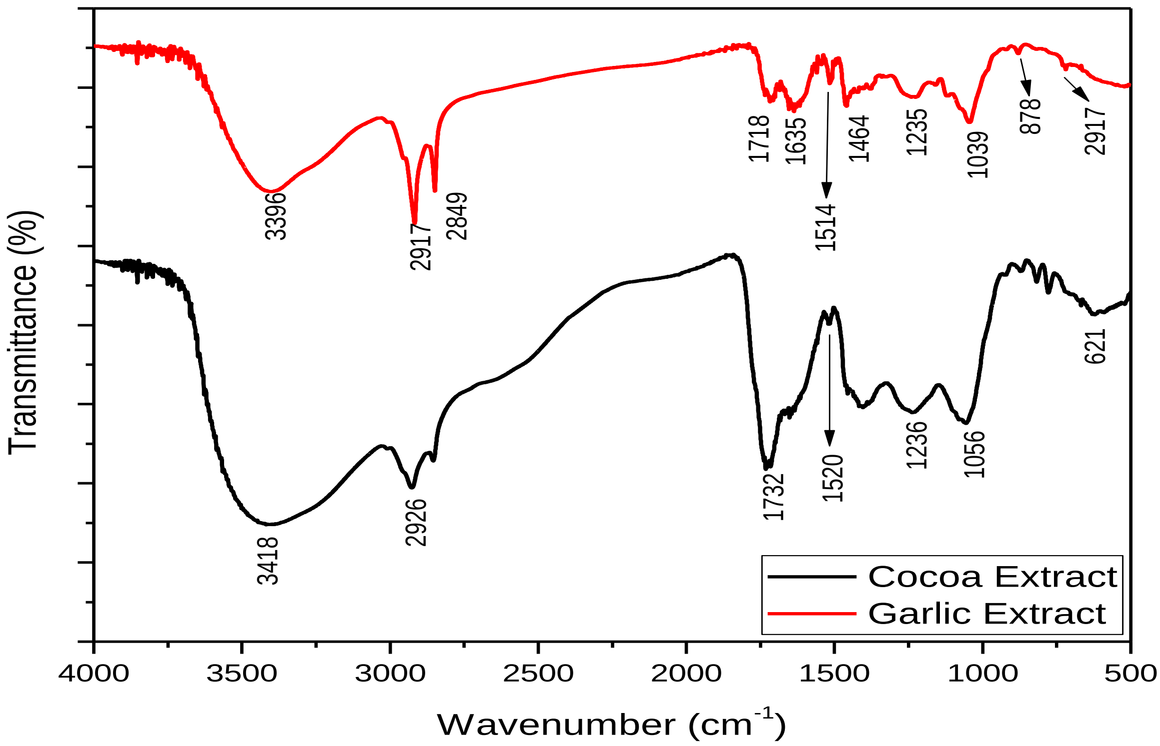
The Fourier transform Infrared spectroscopy (FTIR) was used for chemical characterization of the garlic and cacao peels extracts using the Thermo Scientific Nicolet spectrometer model is10 in the range of wavelength 4000 to 400 cm^{-1}.

3. Results and Discussion

3.1 Infrared spectroscopy in the Fourier transform (FTIR)

Figure 1 shows the FTIR spectra of the garlic and cacao peel.

Figure 1 - Infrared spectra of the sample of cacao peel extract and Infrared spectra of the sample garlic peel extract.



Source: Authors.

The chemical characterization of garlic and cacao peel extract obtained by the FTIR (Fig. 1) showed the presence of some compounds with antioxidant properties, mainly sulfur at 1240 cm^{-1} (SS) and nitrogen at 1636 cm^{-1} (NH) in garlic peel extract and nitrogen at 1520 cm^{-1} (C=N), and at 621 cm^{-1} (NH_3) in the peel cacao extract that can act as corrosion inhibitors for carbon steel, according to what has been observed in the literature (Garai *et al.*,2012)

Nitrogen can act as a corrosion inhibitor (Al-Sabagh *et al*.,2011; Zerga *et al.*,2009*)* and it was found in garlic peel extract (1718 cm^{-1}) and in the cacao peel extract (1520 cm^{-1} and 621 cm^{-1}) respectively. However, the ascribed to súlfur-containing compounds were also detected at 720 cm^{-1} (CS), 1044 cm-1 (S=O) and 1235 cm-1 (SS) are also found in the peel extract of garlic (Fig. 1) and according to Ayeni *et al*., (2014), the sulfur molecule acts as corrosion inhibiting. The band (3396 cm^{-1}) is related to OH, was found in the spectrum of garlic peel extract (Fig 1) and cacao peel extract (Fig.2). The OH band can be related to the presence of ethanol which was not totally eliminated during the extraction process. According to Gomes

(1999), the OH group facilitates adsorption of substances in the metal surfaces because it tends to form hydrogen bonds with the free radicals composed of carbon, nitrogen and sulfur.

Other important bands in this spectrum (Fig. 1) are the ones at 1718 cm^{-1} (C=O), and those between 1240 cm^{-1} and 1636 cm^{-1}, which correspond to organic molecules to organic compounds containing nitrogen and sulfur. Other specific bands ascribed to sulfur-containing compounds were also detected at 720 cm^{-1} (CS), 1044 cm^{-1} (S=O) and 1235 cm-1 (SS) [20]. Gomes (1999), also assigns inhibitive properties to C=O groups for carbon steel. Finally, according to Marzorati, Verotta & Trasatti (2018), organic compounds containing nitrogen and sulfur can act as corrosion inhibitors due to their antioxidant properties.

The FTIR spectrum of the cacao peel extract (Fig. 1) found specific bands ascribed to nitrogen-containing compounds were detected at 1520 cm^{-1} (C=N), and at 621 cm^{-1} (NH3) which these elements can act as a corrosion inhibitor (Alsabagh *et al.*, 2015).

3.2 Gravimetric tests

The inhibition efficiency (*IE*) was determined from gravimetric tests after 2 h of immersion in the different electrolytes. IE was calculated from equation (1), where *W*corr (w/o) and *W*corr (w) correspond, respectively, to the weight loss without and with the inhibitor (Zhao & Chen, 2012):

$$IE = \frac{W_{corr(wo)} - W_{corr(w)}}{W_{corr(wo)}} x100 \quad (1)$$

The results of the weight loss after 2 h of exposure in the electrolyte with or without inhibitors in different concentrations are summarized in Table 1. The results evidence that corrosion process in carbon steel occurs when immersed in 0.5 $mol.L^{-1}$ HCl solution; however, the process is minimized in the presence of the inhibitors. In regard to extract, it can be verified that the inhibiting power increases with the increase of inhibitor concentration. This occurs by the presence of antioxidant molecules in the extracts which are adsorbed in the substrate surface, thus retarding the corrosion process (Gomes, 1999).

It can be verified by n (%) column that with increasing concentration the inhibition efficiency increased, but the cacao peel extract is slightly more efficient than the garlic peel extract. The inhibition efficiency presented in table 1, for garlic peel extract, is the following literature (Pereira & Pêgas, 2012), whereas for the cacao peel extract the efficiency was not found in the literature.

Table 2 - Weight loss of carbon steel – ASTM 1020 after 2 h of immersion in 0.5 $mol.L^{-1}$ HCl solution in the absence and the presence of inhibitors for different concentrations.

Medium	Variation (g)	W_{CORR} ($g.cm^{-2}.h^{-1}$)	*n* (%)
Without inhibitor	1.3×10^{-2}	5.43×10^{-4}	-
S1	2.0×10^{-3}	8.33×10^{-5}	84.12
S2	1.7×10^{-3}	7.08×10^{-5}	86.95
S3	1.0×10^{-3}	4.17×10^{-5}	90.65
S4	9.3×10^{-4}	3.89×10^{-5}	89,00

Source: Authors.

The results obtained from the weight loss test for CS- ASTM 1020, in the absence and presence of the inhibitor synergism in hydrochloric acid medium 0.5 mol.L^{-1} are shown in Table 3.

Table 3 - Weight loss of CS – ASTM 1020 after 2 h of immersion in 0.5 mol.L^{-1} HCl solution in the absence and the presence of inhibitors.

Inhibithors (Synergism)	Variation (g)	W_{CORR} (g.cm^{-2}.h^{-1})	*n* (%)
Without inhibitor	1.30 x10^{-2}	5.43 x10^{-4}	-
S5	7.67x10^{-4}	3.19x10^{-5}	94.12
S6	5.00x10^{-4}	2.08x10^{-5}	96.03
S7	4.00x10^{-4}	1.67x10^{-5}	97.46
S8	2.00x10^{-4}	8.33x10^{-6}	98.13

Source: Authors.

Table 3 shows the performance of corrosion inhibitors from the synergy between garlic and cocoa peel extract that present an efficiency high than 90% independent of the concentration used in the synergism. Comparing the efficiency values for the synergism (table 3) with the garlic and cocoa peel extract (table 2) for the same solution concentration (1.11 g L^{-1}), it is observed the efficiency increase in the synergism indicating that is viable to use the mix of both inhibitors to improve the efficiency. However, it is important to note that the synergism efficiency is an optimized condition for the inhibition effect of garlic and cacao peel extract in which, each one presents a good efficiency inhibition for the CS –ASTM 1020 in HCl solution 0.5 mol.L^{-1}.

These results are higher than the result found in the literature for the same conditions (Ostovari *et al.*, 2009), which showed the efficiency of 92,6 % in the maximum for the henna extract on carbon steel to 1.2 g.L^{-1} of solution concentration. The literature also reports the efficiency in this magnitude due to inorganic inhibitors such as, N-methyl-p-aminophenol sulfate which presents an efficiency of 81.9% in maximum to 27.5 g.L^{-1} solution concentration (Vicent & Okhio, 2005).

Barreto et al. (2018) studied the use of cocoa bark extract for possible substitution of benzotriazole (BTAH) in the inhibition of 1020 carbon steel in hydrochloric acid. The inhibition efficiency calculations from weight loss, EIS, and polarization tests have shown that cocoa bark extract is only slightly less efficient than the BTAH to mitigate corrosion in the aforementioned conditions.

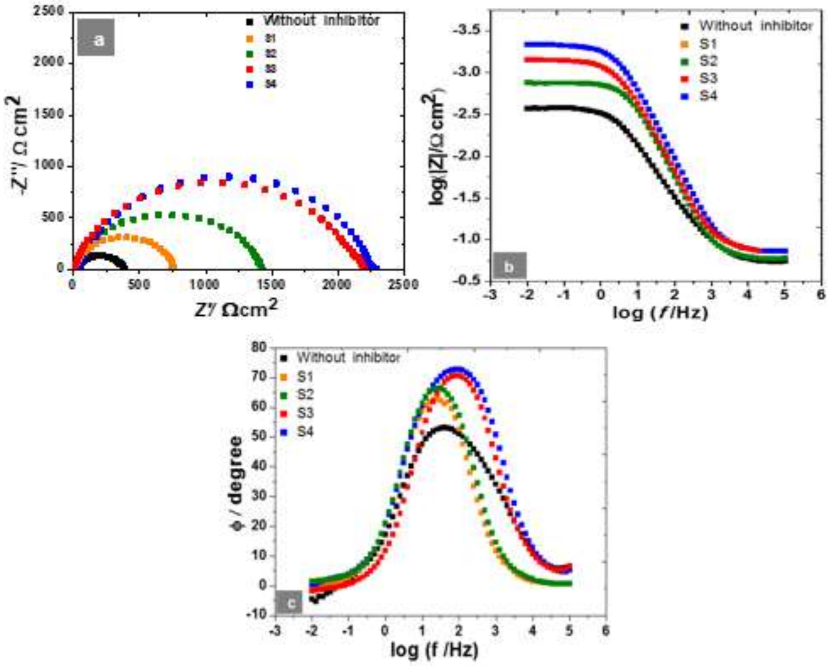
3.3 Electrochemical techniques

3.3.1 Electrochemical impedance spectroscopy (EIS)

This technique was employed seeking more detailed information about the phenomena that occur at the electrode/solution interface, and to confirm results obtained by the technique of polarization.

Figure 3 presents the EIS measurements for the samples in different inhibitors concentrations and without inhibitors obtained after 90 min of open circuit potential (OCP) measurements, in HCl solution 0.5 mol.L^{-1}.

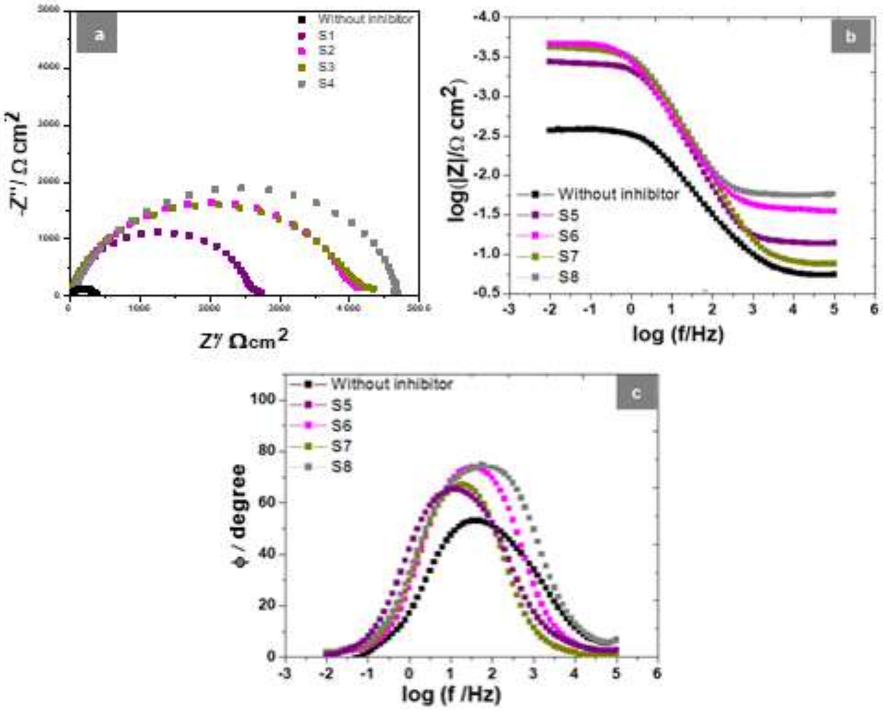
Figure 3 - Nyquist (a) and Bode (b) and (c) diagrams for carbon steel after 90 min of immersion in HCl 0.5 mol.L^{-1} solution in the presence and absence of garlic peel extract and cacao peel extract.



Source: Authors.

Independently of the presence of the inhibitor, the Nyquist diagram is composed of a single depressed capacitive loop, indicating that, whatever the solution composition, the corrosion mechanism remains the same (Zhao & Chen, 2012; Chevalier *et al.*, 2014). The results also show that the addition of the inhibitor to the HCl solution increases the impedance response of CS, indicating enhanced corrosion resistance and that increasing the inhibitor concentration improves the inhibitive effect, being the highest real impedance value to cacao peel extract, as it is observed in the Bode diagram (Figure 3b). On the other hand, the phase angle diagram (Figure 3c) presents a similar phase angle for both inhibitors, indicating a good barrier layer resistance which reduces the evolution of corrosion process. Such improvement in the corrosion resistance may be attributed to increased adsorption of molecules with inhibitory properties on the substrate surface (Babi & Hackerman, 2005; Custódio *et al.*, 2010) forming a more protective layer (Torres *et al.*, 2011) that hinders the evolution of the corrosive process. Figure 4 shows a Nyquist diagram obtained by the EIS in the absence and presence of the inhibitor synergism.

Figure 4 - Nyquist (a) and Bode ((b (c)) diagrams for carbon steel after 90 min of immersion in HCl 0.5 mol.L^{-1} in the presence and absence of inhibitors.



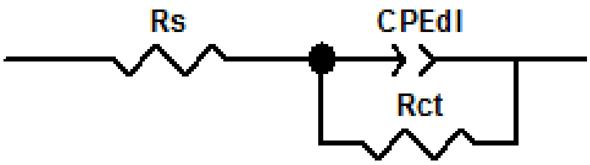
Source: Authors.

Comparing the EIS synergism results (Figure 4) with the garlic and cacao peel extracts (Figure 3) it is noted that the mixture of inhibitors promotes an increase in impedance values improving the inhibitory efficiency of CS-ASTM 1020 in aggressive solution. Additionally, in the presence of the inhibitors, the capacitive response increased, indicating the displacement of charged species from the surface. This fact can be ascribed to the adsorption of the surface-active components of peel garlic extract and cacao to the surface blocking the access of aggressive species and hindering the corrosion reaction (Pereira & Pêgas, 2012; Babi & Hackerman, 2005; Wolynec, 2003).

To have a better quantitative analysis of the impedance behavior, the EIS diagrams of Figure 3 were fitted using an electric equivalent circuit (EEC) (Figure 5) which is usually employed to model the impedance response of steel in acidic solutions without or with inhibitors (Duval *et al.*, 2002; Banerjee, Srivastava & Singh, 2012; Khaled, 2008; Ghailane *et al.*, 2013). In the circuit, R_s stands for the solution resistance, R_{ct} represents the charge transfer resistance and CPE_{dl} is a constant phase element representing the double layer charging, which accounts for frequency dispersion in the EIS response, usually ascribed to physical phenomena as roughness or non-homogeneity of the surface (Ghailane *et al.*, 2013). The impedance of a *CPE* is defined by Eq. (2), where in Q is the *CPE* constant, ω is the angular frequency (rad.s^{-1}), i^2= -1 is the imaginary number and α is the *CPE* exponent (Rajam, Rajendran & Saranya, 2013) Table 3 presents the results of the fitting procedure.

$$Z_{CPE} = Q^{-1}(i\omega)^{-\alpha} \quad (2)$$

Figure 5- Equivalent circuit to adjust the EIS results.



Source: Authors.

The adjustment was performed in the software zview 2.4. The parameters and the inhibitor efficiency obtained are shown in Table 3, where it can compare the results of both inhibitors studied.

Table 3 - The parameters obtained from EIS adjustment.

	Concentration g L^{-1}	R_s [Ω cm^2]	R_{ct} [Ω cm^2]	*CPE-T* [F cm^{-2} $s^{(n-1)}$]	A	*IE%*
Without inhibitor	-	5.5	395	2.6 10^{-4}	0.74	-
S3	1.11	7.2	2100	3.8 10^{-5}	0.88	81.2
S4	1.11	6.9	2117	3.2 10^{-5}	0.87	81.3
S5	1.11	6.9	2624	4.1 10^{-5}	0,67	85.0
S6	1.11	5,8	3905	3.1 10^{-5}	0,95	89.9
S7	1.11	5,8	3670	3.9 10^{-5}	0,41	89,2
S8	2.22	6,3	4784	5.6 10^{-5}	0,52	91.7

Source: Authors.

The double-layer capacitance (Cdl) was calculated using the Equation 3:

$$Cdl = \frac{1}{2\pi . fmax . Rtc} \quad (3)$$

where f_{max} is the frequency and R_{tc} is the charge transfer resistance due to the electric double layer.

In table 3, it can be observed that the R_{tc} values increase in the presence of inhibitors and the C_{dl} values decrease, indicating that the electric double layer acts as a barrier layer for the evolution of corrosive process (Pereira & Pêgas, 2012), due to adsorption of the antioxidants molecules on the CS surface.

The Cdl values for inhibitors have a significant reduction compared to the value obtained in the absence of this, however, the Cdl value decrease more for the sample with inhibitors, although the Cdl values do not present a significant difference between the inhibitors as shown in the bode diagrams (Fig 3 b e c e Fig 4 b e c). The inhibitors efficiency was calculated through equation 4:

$$IE\% = \frac{R_{Tinb} - R_{Tco}}{R_{Tinb}} \times 100 \quad (4)$$

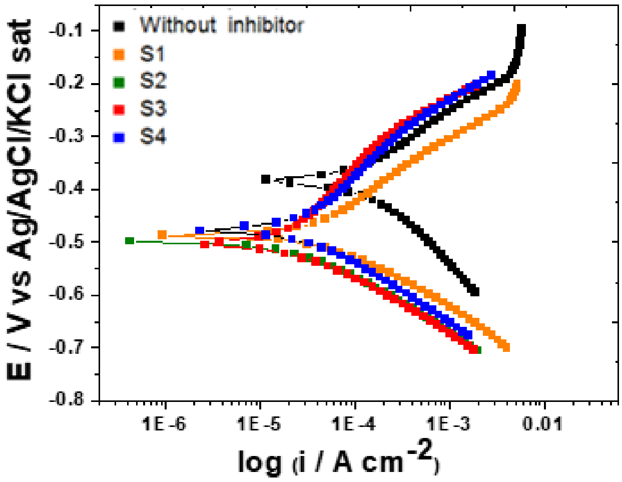
Where R_{Tinb} and R_{Tco} are the charge transfer resistance with and without inhibitor, respectively.

The inhibitor efficiency was calculated from Rtc values with and without inhibitors, all efficiency values exceed 80 %. These results, according to literature, reveal that both inhibitors are good and can be used as corrosion inhibitors because they present efficiency above 70 % (Fadel *et al.*, 2013).

3.3.2 Polarization curves

Figure 6 presents the potentiodynamic polarization curves obtained the absence and in the presence of a different concentrations of the extracts. The results corroborate with the previous tests and show that the addition of the extracts to the test solution reduces CS corrosion and this effect is enhanced with increasing inhibitor amount. They also demonstrate that the inhibitor acts by hindering the cathodic reaction.

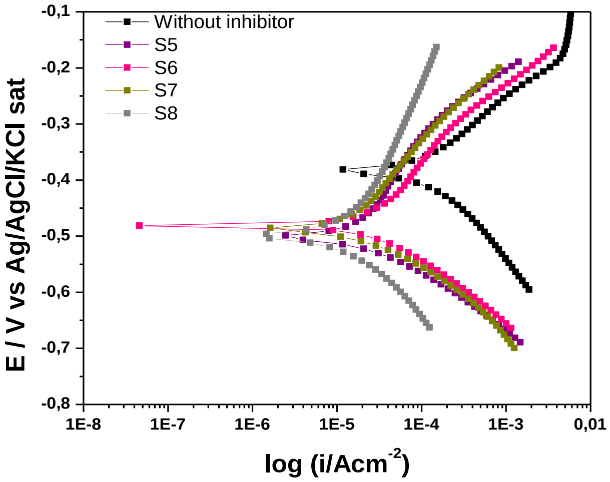
Figure 6 - Polarization curves obtained for ASTM 1020 carbon steel after 110 min immersion in an aqueous solution of 0.5 mol.L^{-1} HCl without and with inhibitors.



Source: Authors.

This result is explained by the adsorption of organic compounds containing sulfur and nitrogen present in garlic peel extract and the nitrogen present in the cacao peel extract which act on the sites of CS-ASTM 1020 minimizing the corrosion process (Fadel *et al.*, 2013; Custódio *et al.*, 2010; Wolynec, 2003). Therefore, the hydrogen reduction reaction is hindered and the corrosion potential is shifted to the negative direction with a consequent diminution of the corrosion current density. The addition of the inhibitors to the electrolyte does not change the cathodic reaction mechanism, just delaying it by the blocking effect, minimizing the hydrogen embrittlement.

Figure 7 - Polarization curves obtained for ASTM 1020 carbon steel after 110min immersion in an aqueous solution of 0.5 mol.L^{-1} HCl without and with inhibitors.



Source: Authors.

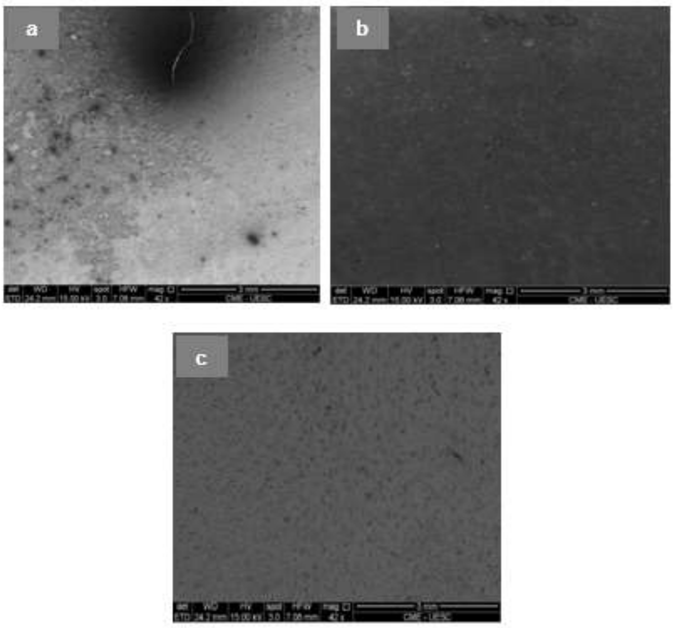
Figure 7 shows potentiodynamic polarization curves Obtained in the 0.5 mol.L^{-1} HCl in the absence and presence of inhibitors mixtures. They show very similar behavior for all inhibitors and confirm all of them act the mixed inhibitors.

3.4 Morphologic characterization

3.4.1 Scanning electronic microscopy (SEM)

The SEM images obtained after 90 min of EIS measurements with and without inhibitor are shown in Figure 8.

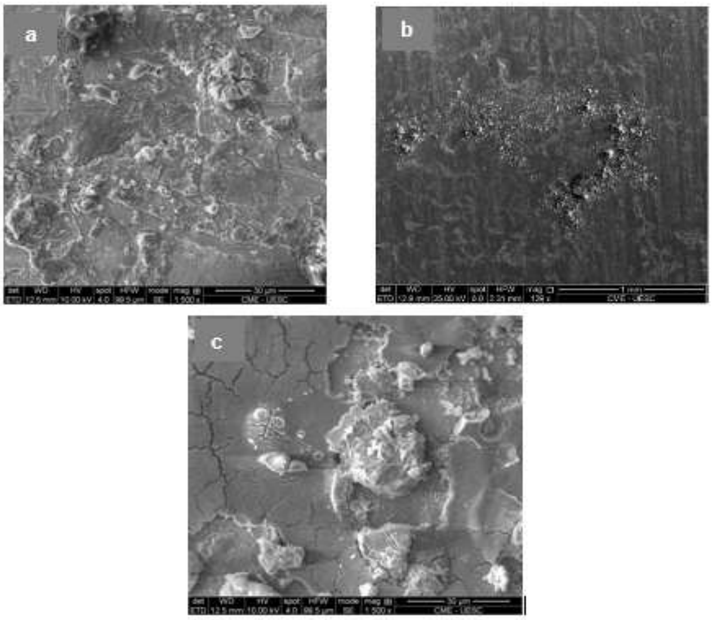
Figure 8 – SEM images for 1020 carbon steel surface obtained after EIS measurements (after 110 min of immersion in HCl solution 0.5 mol.L^{-1}) in the absence of inhibitor (a) in the presence of garlic peel extract (b) in the presence of cacao peel extract (c)



Source: Authors.

The SEM images for the sample without extract (Fig. 8a) present a generalized corrosion process comparing with the samples in the presence of extracts (Fig. 8b and Fig. 8c), indicating that the extracts inhibited the evolution of the corrosion process. In Figures 8b and 8c it is observed that the corrosion process is not uniform indicating that there are defects due to the formation of a protective film result of adsorption of the antioxidant molecules present in the extracts which are not adsorbed uniformly on the carbon steel surface. This probably occurs because of the electrolyte difficulties the reactions between the substrate and the inhibitor molecules maybe because the extracts are not completely dissolved in the electrolyte (Gomes, 1999).

Figure 9 - SEM images for the 1020 carbon steel surface after gravimetric tests in the absence of inhibitor (a) in the presence of garlic peel extract (b) in the presence of cacao peel extract (c).



Source: Authors.

The SEM images for carbon steel with and without inhibitors after gravimetric tests (Fig. 9) shows an attacked area with the formation of corrosion product higher than the samples tested in EIS (Fig.6), showing that the inhibition efficiency of the extracts is smaller for the gravimetric tests than for EIS measurements, proving that the results obtained by both techniques. This result shows that the immersion time can directly influence the inhibition efficiency, as seen in the literature (Duval *et al.*, 2002; Banerjee, Srivastava & Singh, 2012).

4. Conclusion

The results reveal that the peel garlic extract and cacao peel extract have an inhibiting corrosion effect for 1020 carbon steel, in an aqueous solution of HCl 0.5 mol.L^{-1}.The FTIR results of garlic peel extract and cacao peel extract showed the presence of sulfur and nitrogen present in garlic and phosphorus, potassium, sulfur and nitrogen present in cacao. These molecules have the antioxidants properties which have the inhibition characteristic.

In the gravimetric tests, the inhibitory efficiency was 98.13 % for the mixture of inhibitors at 2.22 g.L^{-1}. The electrochemical impedance results in acidic media showed that with increasing inhibitor concentration, higher values of inhibitory efficiency were obtained, with a maximum value of 91.2 % for 2.22 g.L^{-1} the mixture of inhibitors. Electrochemical measurements indicate that the value of the impedance module increases with the addition of the inhibitor in the electrolyte. The SEM images revealed that the formation of the film on the 1020 carbon steel surface delayed the corrosive process due to the inhibitory action of the antioxidants present in the film, as showed by EDS technique, due to the adsorption of these molecules on the carbon steel surface.

The limitation of this work is that residues are from a single region. It is necessary that future works evaluate organic matter from other locations. Furthermore, investigation of other electrolytes is recommended. Finally, it is opportune to characterize the corrosion products that were deposited, in order to verify the changes caused by the inhibitor adsorption process.

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