

Evaluation of Aqueous Coffee Husks Extracts as a Corrosion Inhibitor of 1020 Carbon Steel in 1 mol L⁻¹ HCl Solution

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Corrosive processes in acidic medium reduce the performance and durability of metallic materials, causing problems to several industries. Corrosion inhibitors are commonly used to decrease these effects. As these inhibitors must be ecologically friendly currently, this work evaluated the anticorrosive effect of natural extracts of coffee husks (*Coffea arabica* L.) in the protection of carbon steel in 1 mol L⁻¹ HCl solution. Extractions were performed using water as the extraction solvent. The polyphenols content increased with the extraction temperature, and the extracts were produced using 100 °C. Extract concentrations of 10, 20 and 30 % v/v were analyzed as inhibitors for carbon steel in acid medium, using weight loss and electrochemical tests, as well as scanning electron microscopy. There was an increase in the inhibition efficiency as the extract concentration increased, reaching values around 97 % using 30 %v/v of extract for the weight loss tests.

Keywords: corrosion; natural inhibitors; coffee husks; polyphenol contents; 1020 carbon steel.

1. Introduction

The most widely reported concepts of corrosion are defined as the deterioration of a metallic or non-metallic material, or as the deterioration of the properties of these materials by chemical or electrochemical action of the environment to which they are exposed to¹. One of the most challenging and difficult tasks for the industry is the protection of metals against corrosion, a problem that continues to be of high relevance in a wide range of industrial applications and industrial products, resulting in degradation and eventual failure of components and systems in the industries².

Usually, the reaction processes that trigger corrosion are spontaneous, presenting a chemical or electrochemical feature, and tend to modify the physical-chemical characteristics of the materials. With the increasing world technological advance, the demand for products resistant to corrosion is significant¹.

Among the different methods available to mitigate corrosion, the use of corrosion inhibitors is usually the most appropriate way to achieve this goal³. Due to the increased environmental awareness, the need to develop environmentally friendly processes has been focused on the corrosion inhibiting properties of natural products⁴⁻⁵. This area of research has great importance because, besides of being ecologically sound, non-toxic and mostly biodegradable, agro-industrial products are sources of cheap, readily available, and renewable materials⁴⁻⁶.

Acid solutions are used in the processes of cleaning and pickling of metallic structures, which cause the dissolution of

the metal. The use of corrosion inhibitors is one of the most common methods applied to protect these metals. Toluidines, phenylhydrazines, dibutylamines, and quinolones are some of the organic substances most used in the pickling of carbon steel in the acid medium since the 1930s⁷⁻⁸. Although these substances exhibit excellent corrosion inhibition behavior, they also present high toxicity. Therefore, the development of corrosion inhibitors that may protect the carbon steel and decrease environmental problems are still technologically interesting.

Coffee chemistry is characterized by its richness of components, including carbohydrates, lipids, proteins, caffeine, tannins, and polyphenols⁹. The tannins may lead to the formation of a film on the metal surface, avoiding corrosion¹⁰. The effects of spent coffee grounds extracts on the corrosion of carbon steel in a 1 mol L⁻¹ HCl solution, were examined by electrochemical procedures, weight loss experiments, and surface analysis. The authors showed that the inhibition efficiency increased as the extract concentration and temperature raised, and that these extract acted as a mixed-type inhibitor with predominant cathodic effectiveness⁷. Roasted coffee extracts were also investigated as carbon steel corrosion inhibitors in a 1 mol L⁻¹ HCl solution, providing an efficient inhibitory effect to the substrate¹¹. Recently, lyophilized extracts of coffee husks obtained by 1 h infusion were used as corrosion inhibitors for carbon steel in acid medium. These extracts presented inhibitory efficiency close to 90% after 24h in the corrosive medium¹². However, the time and temperature of the extraction process can affect the polyphenols content of the extract, which may interfere in the anticorrosive performance of the natural inhibitor¹³. Therefore, the goal of the present study was to evaluate

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the effect of the extraction temperature on the polyphenols content of the inhibitor coffee husk aqueous extracts and to study the anticorrosive performance of the extract obtained under this selected condition in the corrosion of carbon steel in 1 mol L⁻¹ HCl solution.

2. Experimental Procedures

2.1 Preparation of steel substrate

Rectangular carbon steel AISI 1020 coupons (2 cm x 1.5 cm x 0.3 cm) were used for electrochemical characterization and weight loss tests. These substrates were polished with emery papers of different granulometry (100, 220, 320, 400, 500 and 600 mesh), then cleaned with water and ethanol, and finally dried in an airflow. For the electrochemical evaluations, the coupons were connected to a copper wire and embedded in resin before polishing.

2.2 Production of the inhibitory extract

Based on earlier used procedures¹⁴⁻¹⁵, the extraction using distilled water was used to perform the experiments. Coffee husks (*Coffea arabica* L.), shown in Figure 1, from the region of Campo Belo (Minas Gerais, Brazil), previously ground in an electric mini-processor (Black & Becker HC31), were used as the matrix for the extracts. The quantities used were weighed in analytical balance (Sartorius TE214S, uncertainty of 0.1 mg). The procedures described here were similar to those used to prepare coffee leaf extracts¹⁵. The aqueous husks extract was produced by weighing approximately 5 g of the previously ground coffee husks to which 150 mL of distilled water was added. Then, this system was conditioned in a thermostatic bath (Nova Técnica) at 60, 80, and 100°C for 30 minutes. Subsequently, the extracts obtained were vacuum filtered and stored in the refrigerator after cooling at room temperature (25°C).



Figure 1. Coffee husks (*Coffea arabica* L.) before being ground.

2.3 Determination of total phenolic compounds

The determination of phenolic compounds total contents, present in the extracts prepared in Section 2.2, was performed using the Folin-Ciocalteu methodology¹⁶. Briefly, sample aliquots of 1.00 mL were pipetted into a 50 mL flask containing 0.5 mL of the Folin-Ciocalteu's reagent, 7 mL of deionized water and 1.5 mL of a 20% w/v Na₂CO₃ solution. The volume was filled with deionized water and heated at 40 °C for 30 minutes.

A standard solution of gallic acid (stock solution of total phenols) was prepared from the dissolution of 0.01 g of gallic acid, weighed on an analytical balance, with 0.1 mg precision, in 1.00 mL of ethanol. Then, the mixture was diluted with deionized water in a 10.00 mL volumetric flask. From this stock solution, standard solutions were prepared with known concentrations of gallic acid to build the calibration curve (5, 10, 15, 25, 50, and 70 µg mL⁻¹). The same procedures described previously for the samples were used to prepare the standard solutions. The absorbance of the standards and samples were measured at 765 nm wavelength using a Camspec M501 Single Beam Scanning UV/Visible Spectrophotometer. The results were expressed as mg of gallic acid equivalents (GAE)/100g of the sample.

2.4 Preparation of the solutions for electrochemical and gravimetric tests

The solutions used for the electrochemical and gravimetric experiments were prepared using a volumetric flask of 100.00 mL, in which volumes of 10.00, 20.00 and 30.00 mL of the inhibitory extracts and 9.3 mL of concentrated hydrochloric acid were added. Thus, extracts with concentrations of 10, 20, and 30% v/v, respectively, in 1.0 mol L⁻¹ HCl solution were produced. For comparison purposes, a solution of 1.0 mol L⁻¹ HCl, without the presence of extracts (blank tests), was also prepared.

2.5 Electrochemical characterization

The electrochemical evaluations were performed in duplicate using a potentiostat/galvanostat (model Autolab PGSTAT 302N). For all experiments, a three-electrode cell was used, at 25 °C: 1020 carbon steel as the working electrode (average exposed area = 1.5 cm²), a saturated calomel electrode as the reference electrode and a platinum spiral, used as the counter electrode. The electrolyte was the acidic solution containing or not (blank test) the inhibitor extracts at concentrations of 10, 20, and 30% v/v, prepared using the extraction procedure described in Section 2.2.

The electrochemical impedance spectroscopy (EIS) tests were carried out after stabilization of the system at open circuit potential (OCP) for 30 min, using a potential sinusoidal perturbation with an amplitude of 10 mV, in a frequency range between 0.001 Hz and 10⁵ Hz. The results were simulated and adjusted using the software Nova Metrohm Autolab. The corrosion inhibition efficiency (IE %) was calculated

using charge transfer resistance (R_{ct}) values, obtained from the EIS tests, according to Equation 1⁷:

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (1)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistances for the system obtained in a 1.0 mol L⁻¹ HCl solution in the presence and absence of the inhibitor, respectively.

The linear polarization resistance (LPR) tests were performed by varying the potential between ± 10 mV around the OCP, with a scanning speed of 0.1 mV s⁻¹, to determine the polarization resistance (R_p) value. Subsequently, potentiodynamic polarization (PP) tests were carried out by varying the potential between ± 500 mV, around OCP. In this case, a scanning speed of 1 mV s⁻¹ was used. Tafel parameters were obtained from the polarization curves using GPES 4.9 software.

IE % values were also calculated using both the corrosion current densities (j_{corr}) obtained from the potentiodynamic polarization curves, by the Tafel extrapolation method (Equation 2)⁷, and the polarization resistance (R_p) values, from the LPR measurements (Equation 3)¹⁷.

$$IE\% = \frac{j_{corr,0} - j_{corr}}{j_{corr,0}} \times 100 \quad (2)$$

$$IE\% = \frac{R_p - R_{p,0}}{R_p} \times 100 \quad (3)$$

In Equation 2, $j_{corr,0}$ and j_{corr} are the corrosion current density values obtained for the system in the absence and the presence of the inhibitor extract, respectively. Similarly, in Equation 3, $R_{p,0}$ and R_p are the polarization resistance values obtained for the system immersed in the corrosive medium, respectively in the absence and presence of the extracts.

2.6 Weight loss experiment

The weight loss experiments were performed at 25°C, for four hours, by immersing the specimens (average area = 6 cm²) in acidic solutions, prepared in the absence and presence of aqueous extract at 10, 20 and 30% v/v. The specimens were removed, rinsed with water, ethanol and dried with warm air. The mass loss was determined gravimetrically using an analytical balance (Sartorius TE214S), with a precision of 0.1 mg. The inhibition efficiency was calculated using Equation 4¹⁵.

$$IE\% = \frac{W_0 - W}{W_0} \times 100 \quad (4)$$

where W_0 and W are the corrosion rates of carbon steel (mm/year), in the absence (blank test) and presence of the extract, respectively, which were calculated using Equation 5¹⁵.

$$W = \frac{\Delta m \times 87600}{A \rho t} \quad (5)$$

where Δm is the difference between the initial and final mass of the sample, A is the specimen area, ρ is the carbon steel density, and t is the immersion time.

2.7 Morphological characterization

Scanning electron microscopy (SEM) was performed, using a JEOL/EO JSM-6510, Version 1.0 microscope, to evaluate the surface morphology of the selected specimens obtained from the weight loss experiment. Before the analysis, the samples were cleaned with alcohol, dried with warm air, and adapted to the stub. The analysis was carried out using secondary electron mode (SE), with beam acceleration of 20 kV and magnification of 5000X.

2.8 Stability of the inhibitory ability of the extracts

The stability of the inhibitory ability of the coffee husk extracts was performed by evaluating the Nyquist diagram of the steel in HCl 1 mol L⁻¹ solution, in the presence and absence of 30 % v/v of extract, after 24 h of exposure to the corrosive medium. The EIS experiment was performed under the same conditions used in Section 2.5, and the EIS data were simulated using the same software earlier mentioned.

3. Results and Discussion

3.1 Total polyphenolic compounds in the coffee husks extracts

Polyphenolic compounds and alkaloids are substances usually found in coffee samples and are generally considered as the main antioxidant substances present in extracts of natural products⁷. Table 1 shows the total phenolic concentration in the coffee husk aqueous extracts prepared at temperatures of 60, 80 e 100 °C. It can be noted that the total phenolic concentration increased with the extraction temperature. This result agrees with the work of Bassani et al.¹⁸, using roasted yerba-mate leaves extracts. The present result suggests that 100 °C is the best working temperature to produce coffee husks inhibitory extracts, as more polyphenolic compounds were released under this condition.

Table 1. Total phenolic content of aqueous coffee husks extract, at temperatures of 60, 80 e 100°C.

Temperature (°C)	Total phenolic (mgEAG/100g of extract)
60	222.135
80	289.735
100	495.401

3.2 Electrochemical impedance spectroscopy (EIS): effect of the extraction temperature.

Figure 2 presents the Nyquist diagram of carbon steel in HCl 1 mol L⁻¹, in the presence of 30% v/v coffee husk aqueous extracts, prepared at temperature of 60, 80, and 100 °C.

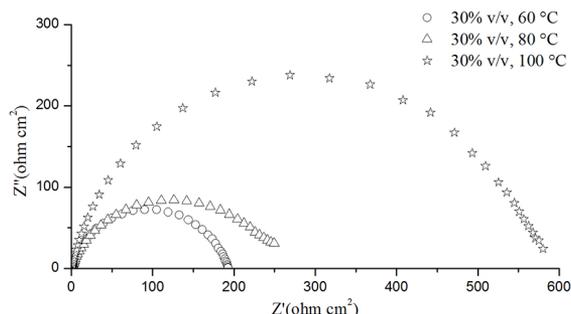


Figure 2. Nyquist diagram of carbon steel in HCl 1 mol L⁻¹, in the presence of 30% v/v coffee husk aqueous extracts, prepared using extraction temperatures of 60, 80 and 100 °C.

Considering that the capacitive semicircle diameter as a qualitative parameter related to the corrosion resistance⁸, a higher semicircle diameter was observed for the experiment performed using the extract produced at 100 °C, probably due to the higher polyphenol contents found in this extract (Table 1). These results are in agreement with the total polyphenol contents in the extract. Therefore, under the conditions used in the present work, 100 °C was selected as the temperature to produce the coffee husks aqueous extract and to evaluate its inhibitory effects on the corrosion of carbon steel in HCl 1 mol L⁻¹.

3.3 Electrochemical impedance spectroscopy (EIS): effect of the extract concentration

Figure 3 presents the Nyquist diagram of carbon steel in HCl 1 mol L⁻¹, in the absence and presence of coffee husk aqueous extracts prepared at 100 °C.

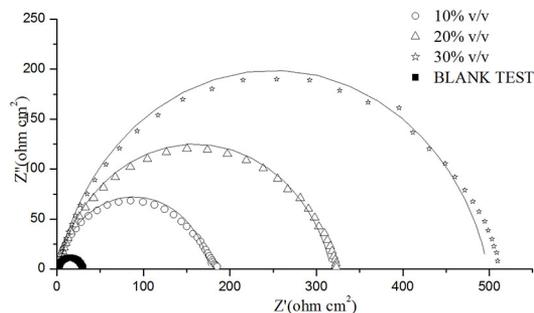


Figure 3. Nyquist diagram of carbon steel in HCl 1 mol L⁻¹, in the absence and presence of coffee husk aqueous extracts, prepared using extraction temperature of 100 °C, at different concentrations.

It can be noted that the addition of the coffee husk extracts to the corrosive medium increased the semicircle diameter, compared to that obtained for the blank test. Based on this characteristic, it can be inferred that this extract acted as corrosion inhibition of the carbon steel in the studied medium, confirming the extractions of antioxidant substances, responsible for the inhibitory process. Similar results were found in the literature for other natural inhibitors, as coffee leaves¹⁵ and roasted coffee¹¹ extracts in 1 mol L⁻¹ HCl solution.

Figure 3 also shows that the increase in the extract concentration enhances the corrosion resistance of the carbon steel in the studied medium, as the diameter of the Nyquist diagrams increased with this parameter. As the extract concentration in the aggressive medium increases, it is expected that the polyphenols content also rises, contributing to the anticorrosive performance of the coffee husks extract.

It is possible to see that only one semicircle was verified for the Nyquist diagrams obtained for the medium containing the aqueous extracts (Figure 3), indicating that only one time constant is present under this condition, independent of the extract concentration used. Therefore, the data obtained in the EIS tests were simulated, using the equivalent electric circuit model presented in Figure 4. In this circuit, R_s represents the solution resistance, R_{ct} is the charge transfer resistance, and CPE represents the constant phase element associated with the electrical double layer capacitance. The simulation adjustment was considered satisfactory for an error value of less than 1%¹⁹. The curves resulting from these simulations are also presented (full line) in Figure 3.

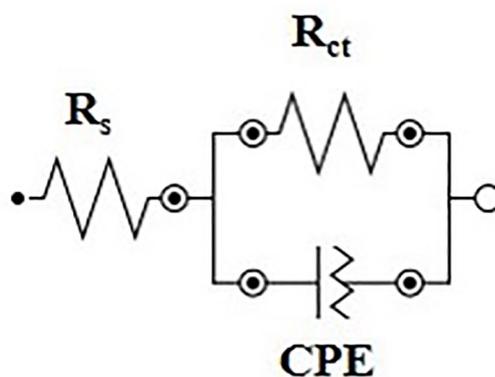


Figure 4. Equivalent electric circuit model.

Based on these simulations, it was possible to determine the charge transfer resistance (R_{ct}), which is shown in Table 2, as well as the IE % values calculated using Equation 1 (Section 2.5). The electric double-layer capacitance (C_{DL})²⁰ was calculated based on the constant phase element (CPE) by using Equation 6²⁰. The C_{DL} results, along with the fitting errors obtained for each parameter in the simulation, are also shown in Table 2.

Table 2. Parameters obtained after the simulation of the EIS data for 1020 carbon steel in 1 mol L⁻¹ HCl solution, in the absence and presence of aqueous coffee husks extracts, at different concentrations. The IE% results are also shown in this table.

Experiments	R _{ct} (ohm cm ²)	R _{ct} (%) [*]	CPE (Mho)	CPE (%) [*]	η	η (%) [*]	R _s (ohm cm ²)	R _s (%) [*]	χ ²	C _{DL} (F cm ⁻²)	IE%
10% v/v	174.72	0.609	1.80E-04	1.795	0.879	0.267	1.10	0.745	0.034	5.56E-05	83.40
20% v/v	316.26	0.667	1.11E-04	1.764	0.853	0.268	1.37	0.855	0.038	2.44E-05	90.83
30% v/v	497.25	0.892	8.57E-05	2.119	0.859	0.32	1.29	1.185	0.068	1.92E-05	94.17
Blank Test	29.01	0.399	3.16E-04	1.694	0.859	0.263	1.22	0.395	0.011	8.63E-05	-

*Estimated error

$$C_{DL} = CPE^{\frac{1}{N}} x \left[\frac{(R_s x R_{ct})}{(R_s + R_{ct})} \right]^{\frac{1-N}{N}} \quad (6)$$

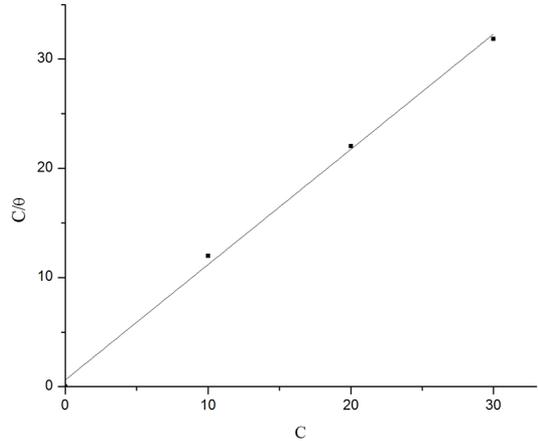
Higher R_{ct} and lower C_{DL} values indicate a system with higher corrosion resistance, high IE % values, and greater inhibitory capacity²¹. The results presented in Table 2 confirm the observations from the Nyquist diagram (Figure 3), since the R_{ct} values increased in agreement with the concentration of the extracts, while the C_{DL} values decreased in the same direction. In these cases, the best results were obtained for the conditions where 30 % v/v of the inhibitory extract was added to the corrosive medium. As expected, Table 2 shows that the IE % values also increased with the extract concentration, and 94.17% was obtained for the experiment using 30 % v/v of the inhibitory extract.

Inhibition efficiency is directly proportional to the fraction of the surface covered by adsorbed molecules (θ)²², which was calculated using the R_{ct} data obtained from the electrochemical impedance diagrams. The variation of θ with the extract concentration specifies the adsorption isotherm that describes the system. The fit of the obtained data to the Langmuir isotherm is illustrated by plotting C/θ versus C, according to Equation 7²²:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (7)$$

where K is the adsorption equilibrium constant. Figure 5 displays the linear plot with a high R² value (0.99647) and a slope of 1.056, which is consistent with the formation of a protective monolayer on the metal surface with a fixed number of adsorption sites¹². This behavior suggests that the compounds present in the coffee husk extract were adsorbed onto the carbon steel surface according to a Langmuir adsorption isotherm²².

A comparative analysis is inappropriate if the molecular mass of the components responsible for the adsorption process is unknown. Consequently, it is not possible for the present work to discuss adsorption isotherm behavior in terms of thermodynamic parameters such as the standard free energy of adsorption value to support the use of natural product extracts as inhibitors²³.


Figure 5. Langmuir adsorption isotherm of aqueous coffee husk extract on the carbon steel surface in HCl 1 mol L⁻¹.

3.4 Evaluation of the inhibitory effect of the extracts: comparative analyses

The inhibitory effect of the coffee husks extracts, obtained at 100 °C, on the carbon steel sample exposed to the acid medium was also evaluated using other electrochemical techniques, as well as by weight loss measurements. These experiments aimed to compare the IE % values obtained among all the different techniques used.

3.4.1 Linear polarization resistance (LPR)

Table 3 shows the LPR tests results for the carbon steel immersed in the corrosive medium used in this work, in the absence and presence of the inhibitor aqueous extracts. As expected, it can be verified that the R_p values increased as the extract concentration in HCl 1 mol L⁻¹ was raised. Although it is possible to consider that, both the R_{ct} and the R_p results could be related to the resistance of the steel electrode to overcome polarization in the studied medium, it is necessary to remember that these analyses are carried out using different AC and DC methods (EIS and LPR, respectively). Therefore, it is always valid to perform both experiments and evaluate their results. The values of IE %, obtained from Equation 3 and presented in Table 3, show that the experiments containing 30% v/v of inhibitory extract presented that the best results, confirming the results earlier seen in the EIS experiments (Table 2).

Table 3. LRP experiments results for carbon steel in 1 mol L⁻¹ HCl medium, in the absence and presence of aqueous coffee husks extracts, at different concentrations.

Experiments	R _p (ohm)	IE %
10% v/v	160.17	86.30
20% v/v	263.10	91.66
30% v/v	421.00	94.79

3.4.2 Potentiodynamic polarization (PP)

Figure 6 shows the polarization curve for carbon steel in 1 mol L⁻¹ HCl, in the absence and presence of coffee husks aqueous extracts, at different concentrations. The electrochemical parameters (corrosion potential (E_{corr}), corrosion current density (j_{corr}), and the anodic (β_a) and cathodic (β_c) Tafel constants), obtained by Tafel extrapolation, can be seen in Table 4. This table also shows the IE % values obtained for this technique, using Equation 2.

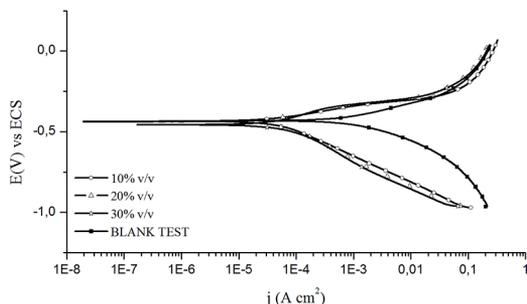


Figure 6. Polarization curve for carbon steel in 1 mol L⁻¹ HCl, in the absence and presence of coffee husks aqueous extracts, at different concentrations.

Table 4. Electrochemical parameters obtained from Tafel extrapolation of the polarization curves of carbon steel in 1 mol L⁻¹ HCl medium in the absence and presence of aqueous coffee husks extracts, at different concentrations. The IE% results are also shown in this table.

Experiments	E _{corr} (V)	β _a (V/dec)	β _c (V/dec)	j _{corr} (A/cm ²)	IE%
10% v/v	-0.436	0.091	0.058	2.49E-05	92.82
20% v/v	-0.437	0.092	0.063	2.88E-05	91.72
30% v/v	-0.458	0.087	0.085	2.63E-05	92.43
Blank Test	-0.429	0.073	0.067	3.47E-04	-

The potentiodynamic polarization curves (Figure 6) show that the extracts caused a decrease in both cathodic and anodic current densities and, apparently, few modifications in the E_{corr}. Table 4 shows that the j_{corr} values obtained in the experiments containing the inhibitory extracts decreased when compared to the blank test, confirming that these extracts act as corrosion inhibitors for carbon steel in HCl 1 mol L⁻¹ medium. The IE % (calculated using Equation 2) had similar values, around 92%, for all the concentrations.

The potentiodynamic polarization curves (Figure 6) show that the extracts caused a decrease in both cathodic and anodic current densities and, apparently, few modifications in the E_{corr}.

Table 4 shows that the j_{corr} values obtained in the experiments containing the inhibitory extracts. It is also seen in Table 4 that E_{corr} shifted to more negative values in the experiments performed in the presence of the coffee husk extracts when compared with the blank test. It is usual to classify the corrosion inhibitors as cathodic or anodic type if the displacement in corrosion potential is more than ±85 mV, in comparison to corrosion potential of the same substrate immersed in a medium without inhibitory substances²⁴. As the shifts in the E_{corr} values shown in Table 4 are smaller than ±85 mV, the coffee husk extract can be characterized as a mixed-type inhibitor. Nevertheless, predominant cathodic effectiveness can be noted for the experiments using the aqueous extracts, as shown in the β_c values shown in Table 4. These results suggest that, under the present conditions, the extracts can retard the main reactions that occur in anodic and cathodic branches: the metal dissolution and the reduction of hydrogen ions to H₂ (g)²⁵, respectively.

3.4.3 Weight loss experiments

The corrosion rate (W) of the 1020 carbon steel in 1 mol L⁻¹ HCl, in the absence and presence of the inhibitory extracts of coffee husks, and the inhibition efficiency of these experiments, calculated using Equation 5 and 4, respectively, are shown in Table 5.

Table 5. Corrosion rates (W) and IE% data for carbon steel in 1 mol L⁻¹ HCl, in the absence and presence of aqueous coffee husks extracts, at temperature of 25°C, using an immersion period of 4 h.

Experiments	W (mm/year)	IE %
10% v/v	2.028	93.92
20% v/v	1.487	95.54
30% v/v	1.099	96.71
Blank Test	33.381	-

As observed in the electrochemical experiments, the highest IE % (calculated using Equation 4) values were found for conditions where 30% v/v of extract was added to the corrosive medium. The W values decreased when the extract concentration increased, and the best IE % result were obtained for the medium containing 30% v/v of the inhibitory extract, confirming the electrochemical results. The IE % results obtained in the present work using this methodology were higher than that reported in the literature for the lyophilized coffee husks aqueous extracts, for the same immersion time¹².

3.5 Surface analysis

As verified in the electrochemical experiments and the weight loss tests, the highest IE% values were found when 30% v/v of the coffee husks extracts were added to the corrosive medium. Therefore, Figure 7 presents the surface morphology of carbon steel before (Figure 7A) and after weight loss tests, performed in acid solution in the absence of extract (Figure 7B), and the presence of 30% v/v of the aqueous extract (Figure 7C). The magnification used was 5000x.

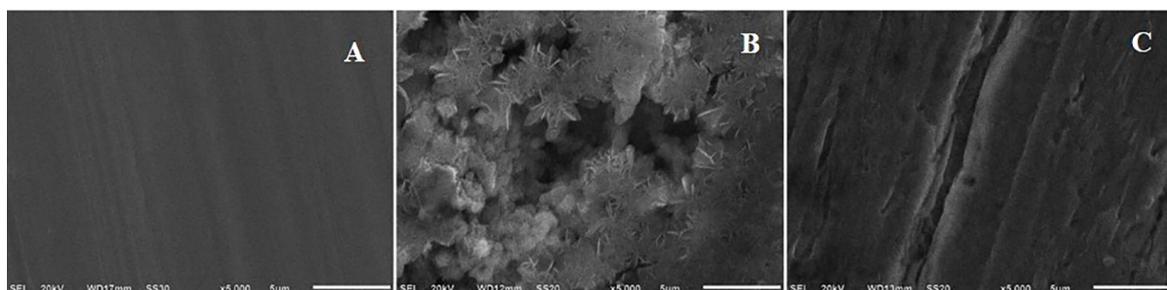


Figure 7. SEM photograph (5000x) of carbon steel before weight loss test (A), after the test, immersed in 1 mol L⁻¹ HCl medium in the absence (B) and presence of aqueous extracts at concentration of 30% v/v (C).

Compared to the polished steel surface (Figure 7A), Figure 7B shows a rough surface, with the presence of pores, characteristic of uniform surface corrosion in acidic medium¹¹. On the other hand, a smoother surface can be noted when the specimen was immersed in the corrosive medium containing the natural extract (Figure 7C). These results indicate that the steel surface was protected by the inhibitory extract, which is in agreement with the electrochemical and weight loss results previously presented. It is possible to verify, therefore, that the coffee husks extracts, produced using the thermostatic bath at 100°C, acted as corrosion inhibitor for the carbon steel in a 1mol L⁻¹ HCl medium.

3.6 Stability of the inhibitory ability of the extracts

Based on the present results, the inhibitory effect of the coffee husk extract on the corrosion of carbon steel substrate in acidic medium was also evaluated by EIS after 24 h of exposure to the corrosive medium, in the presence and absence of 30 % v/v of extract in HCl 1 mol L⁻¹. The results, presented in Figure 8, show a decrease in the capacitive loop after the 24 h of exposure, when compared to the experiments performed after 30 min of immersion, indicating a trend of decreasing the inhibitory ability with exposure time, probably due to the degradation of the phenolic compounds in this period. The IE % values, calculated using Equation 1 and presented in Table 6, for the experiments performed after 24 h of immersion, shows the effects of the extract degradation. However, the R_{ct} value (shown in the same table) for the system immersed in the extract-containing medium after 24 h, was

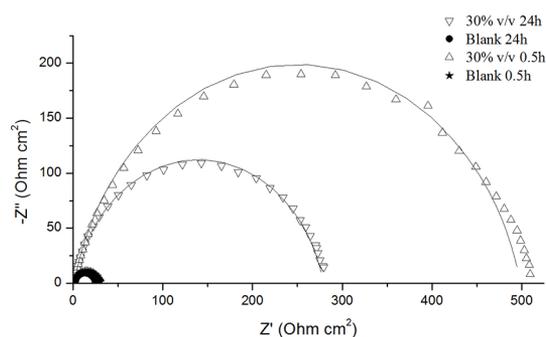


Figure 8. Nyquist diagram of carbon steel after 0.5 h and 24 h of exposure to the corrosive medium, in the presence and absence of 30% v/v of extract in HCl 1 mol L⁻¹.

still higher than the value obtained for the steel exposed to the same medium without the inhibitor extract, under the same conditions, and an IE% value of approximately 91% was obtained. These results indicate that although the extract can still provide suitable protection to the steel substrate after 24 h of exposure in the studied aggressive medium, it is necessary a long-term evaluation to verify a possible schedule to periodically reset this inhibitor in the system to guarantee its maximum inhibitory efficiency.

4. Conclusions

The extraction temperature affected the polyphenol content in the produced aqueous coffee husk extracts. This effect was reflected in the corrosion resistance verified for the carbon steel in acid medium containing the extracts and T = 100 °C was selected to be used as the extraction temperature to the evaluation of the inhibitory effect of these extracts.

Table 6. Parameters obtained after the simulation of the EIS data after 0.5 h and 24 h of exposure to the corrosive medium, in the presence and absence of 30 % v/v of extract in HCl 1 mol L⁻¹. The IE% results are also shown in this table.

Experiments	R_{ct} (ohm cm ²)	R_{ct} (%) [*]	CPE (Mho)	CPE (%) [*]	η	η (%) [*]	R_s (ohm cm ²)	R_s (%) [*]	χ^2	C_{dl} (F cm ⁻²)	IE%
30% v/v 24 h	277.70	0.808	2.43E-04	1.973	0.867	0.303	1.55	0.835	0.042	7.24E-05	91.36
Blank Test 24 h	24.00	0.361	2.55E-03	1.459	0.84	0.295	1.64	0.383	0.010	8.88E-04	-
30% v/v 0.5 h	497.25	0.892	8.57E-05	2.119	0.859	0.320	1.29	1.185	0.068	1.92E-05	94.17
Blank Test 0.5 h	29.01	0.399	3.16E-04	1.694	0.859	0.263	1.22	0.395	0.011	8.63E-05	-

*Estimated error

The electrochemical, weight loss results, and the morphological analysis showed that the inhibition efficiency (IE %) increased when coffee husk extracts were added to the corrosive medium. The increase in the extract concentration enhanced the anticorrosive performance of the carbon steel in this medium, and the best results were obtained when 30% v/v of the extract was used. Polarization studies also showed that the coffee husk extract could be classified as a mixed-type inhibitor, with predominant cathodic effectiveness. The adsorption process occurred according to a Langmuir adsorption isotherm, suggesting the formation of a monolayer after approximately 2 h of exposure in the corrosive medium.

The morphology of the steel surface after immersion in the corrosive medium containing 30 % v/v of the extract confirmed that the corrosion process was decreased under this condition. After 24 h of exposure to this medium, however, there is a decrease in the charge transfer resistance and the IE % values. Nevertheless, the present results suggest that the corrosion process in steel is still decreased in the extract-containing medium after this period of immersion.

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