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Grape Pomace Extracts as Green Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solutions

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The inhibitive action of grape pomace extracts against the corrosion of C-steel in a 1 mol L^{-1} HCl solution was investigated using electrochemical impedance spectroscopy, potentiodynamic polarization curves, weight loss measurements and surface analysis. Hydroalcoholic extracts of grape pomace were analyzed in different concentrations and were found to act as effective corrosion inhibitors for the tested system. The inhibition efficiency increased with increasing extract concentration and decreased with temperature. The adsorption of components of the grape pomace extracts on the surface of the C-steel followed the Langmuir adsorption isotherm.

Keywords: C-steel; EIS; polarization; weight loss; natural products; by-product

1. INTRODUCTION

Acid solutions are widely used in industry, and some of the most important fields of application are acid pickling, chemical cleaning and processing, ore production, and oil well acidification [1-2]. C-steel is one of the most important alloys being used in a wide range of industrial applications.

Corrosion problems arise as a result of the interaction between the aqueous solutions and C-steel, especially during the pickling process in which the alloy is brought in contact with highly concentrated acids. This process can lead to economic losses due to the corrosion of the alloy [3].

The use of inhibitors is one of the most practical methods for protecting against corrosion, especially in acid descaling bathes, to prevent not only metal dissolution but also acid consumption [4]. Inhibitors protect the metals by effectively adsorbing on its surface and blocking the active sites for metal dissolution and/or hydrogen evolution, thereby hindering overall metal corrosion in aggressive environments [5]. Recently, many research studies have been focused on natural extracts that can replace synthetic compounds [6-12]. However, there are few studies focusing on the use of by-products as green corrosion inhibitors. Studies have been conducted on using the following by-product extracts as corrosion inhibitors for C-steel in acidic media: banana peel [13], fruit peel (orange, mango, passion fruit and cashew) [14], coffee grounds [15], mango and orange peel [16], papaya seed [17], peel and seeds from papaya [18] and garlic peel [19]. The use of industrial wastes as corrosion inhibitors, such as peels and seeds is, indeed, very appealing.

Grape pomace is an industrial waste from wine and juice processing, and it primarily consists of grape seeds, skin and stems (~18–20 kg/100 kg of grapes) [20-22]. Flavonoids- anthocyanidins, flavonol, flavanol and tannins – and non-flavonoids, such as phenolic acids derived from cinnamic and benzoic acids and stilbenes are the major phenolic constituents of grape pomace [23-24]. Most part of the 59.4 million kg of grape pomace formed by Brazilian wineries is treated as a low added-value residue, and is used as animal feed and manure. Over the past few years, by-products of wine and grape juice processing have attracted considerable attention as a potential cheap source of bioactive phenolic compounds, which have antioxidant properties and could be used in the pharmaceutical, cosmetic and food industries [25-26]. Therefore, the use of this residue as a valuable winery by-product might promote significant economic gains and prevent or decrease environmental problems caused by grape pomace accumulation [25].

This paper reports the effect of grape pomace extracts as corrosion inhibitors for C-steel in 1 mol L^{-1} hydrochloric acid, using anodic and cathodic polarization curves, electrochemical impedance measurements and weight loss measurements. The test coupon surfaces were analyzed using scanning electronic microscopy (SEM). The effect of temperature was also studied. The grape pomace hydroalcoholic extracts were characterized by Fourier transform infrared spectroscopy, total phenolic content and antioxidant activity.

2. EXPERIMENTAL

2.1. Preparation and characterization of grape pomace extracts

The grape pomace from white wine making kindly provided by Aurora Winery (Bento Gonçalves / RS) was previously rehydrated in distilled water, in a solid:liquid ratio of 2:1, for one hour at 30 °C. Antioxidant compounds were extracted at a 1:9 ratio (w/v) with 30% (v/v) ethanol:water solution, acidified to pH 3.8 with citric acid, mechanically agitated at 48 rpm, and at 50 °C for 120 minutes in a jacketed pan. The crude extract was separated in rotating centrifuge baskets, at 37.5 × *g* equiped with a nylon filter with average porosity of 150 µm. This crude extract was concentrated in a nanofiltration pilot system to achieve a volumetric concentration factor of 8. Both the crude extract and the 8-fold concentrated extract from grape pomace were stored at 4 °C until analysis.

The extracts were analyzed for total phenolic content as proposed by Singleton and Rossi (1965) [27] and modified by George et al. (2005) [28], employing the Folin-Ciocalteau reagent and calibration curves of gallic acid. The results were expressed in mg of gallic acid equivalent (GAE) per 100 g of sample (mg GAE/100 g). Antioxidant activity of the extracts was assessed by the spectrophotometric method described by Re et al. (1999) [29], through reduction of the ABTS radical, and using Trolox® as standard. The results were expressed in µmol of Trolox equivalents (TE) per 1 g of sample. The reaction mechanism in this assay allows the assessment of the antioxidant activity through single electron transfer reactions.

The liquid extracts were characterized by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra, which extended from 4000 to 400 cm^{-1}, were recorded in a Nicolet Magna-IR 760 spectrophotometer using the KBr disk technique.

2.2. Specimen preparation

Working electrodes were prepared from steel specimens with a composition (in wt %) of C: 0.095, P: 0.018, Mn: 0.48, S: 0.0073 and Fe: balance. Coupons cut with 4.0 cm x 2.0 cm x 0.15 cm dimensions were used for weight loss measurements, and specimens prepared by embedding steel rods in epoxy resin with 1 cm^2 of exposed surface area were used as working electrodes for polarization and EIS measurements. The exposed area was mechanically abraded with 400, 500 and 600 grade emery paper, washed with double distilled-water, degreased with acetone and finally dried before each experiment.

2.3. Solution preparation

The electrolyte was a 1 mol L^{-1} HCl solution prepared using double-distilled water. All chemicals were of analytical-grade. The experiments were carried out under non-stirred and naturally aerated conditions. The concentration range of crude and concentrated grape pomace extracts used varied from 0.5 to 3% (v/v) in the electrolyte solution.

2.4. Electrochemical procedure

Electrochemical measurements were carried out using a conventional three-electrode cylindrical glass cell at 25 ± 2 °C. A saturated calomel electrode (SCE) and a large-area platinum wire were used as the reference and auxiliary electrodes, respectively.

Before each electrochemical measurement, the open-circuit potential (OCP) was recorded as a function of time for up to 30 min. After 30 min a steady-state OCP, corresponding to the E_{corr} of the working electrode, was obtained. Electrochemical impedance measurements were carried out using AC signals with a peak-to-peak 10 mV amplitude within the frequency range from 10 kHz to 10 mHz. The impedance diagrams were given by the Nyquist and Bode representation. After the electrochemical impedance measurements, anodic and cathodic polarization curves were obtained separately at a 0.333 mV s^{-1} scan rate in the anodic and cathodic directions ($E = E_{corr} \pm 300$ mV). The above procedures were repeated for each concentration of inhibitors.

The electrochemical experiments were performed using a computer-controlled instrument, Autolab Potentiostat/Galvanostat (PGSTAT30), with GPES and FRA software provided by Autolab used for polarization curves and impedance measurements, respectively.

The inhibition efficiency (IE%) was calculated as follows:

$$IE\ (\%) = \frac{R_{ct} - R_{ct,o}}{R_{ct}} \times 100 \qquad (1)$$

where $R_{ct,o}$ and R_{ct} are the charge transfer resistances in the absence (blank) and presence of the inhibitor, respectively.

2.5. Weight loss measurements

Duplicate specimens were immersed in the acid test solutions in the absence and presence of 2% extracts for 4 and 24 h at room temperature (25 °C). The specimens were then removed, rinsed with water and acetone, dried and finally stored in a desiccator. The weight loss was determined on an analytical balance with at the nearest 0.1 mg. The inhibition efficiency was obtained using the equation:

$$W_{corr}\ (\%) = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

where W_0 and W are the weight losses in the absence (blank) and presence of the extract, respectively.

The effect of temperature on the corrosion rate of steel coupons in a 1 mol L^{-1} HCl solution at 40 and 60 °C was also studied with the same concentration of the extract for immersion periods of 4 h. The measurements of weight loss were obtained according to ASTM G31-72 [30].

2.6. Surface analysis

The specimens used for the surface analysis examination were immersed in 1 mol L^{-1} HCl in the absence and presence of 2% extracts for 4 h at 25 °C. The morphology analysis was performed on a Leo 940A (ZEISS) scanning electronic microscope. The accelerating voltage was 20 kV.

3. RESULTS AND DISCUSSION

3.1. Characterization of grape pomace extracts

FT-IR has been used previously as an important source of information for evaluating the composition of wine [31-34]. Figure 1 shows the FT-IR spectra of crude (A) and concentrated (B) grape pomace extracts. The strong band at approximately 3440 cm^{-1} can be associated with O–H stretching of the phenolic group. The band at 2981 cm^{-1} is related to C–H stretching vibration. The strong band at 1640 cm^{-1} is assigned to conjugated C=O stretching vibration [35]. The band at 1452 cm^{-1} can be attributed to C=C-C aromatic ring stretching [31, 35]. The bands between 1310 and 1390 cm^{-1} can be attributed to angular deformations of C-O-H in phenols. The band at approximately 1273 cm $^{-1}$ is attributed to C-O stretching from the pyran-derived ring structure present in the flavonoids [31-32]. The bands at 1045 and 1087 cm $^{-1}$ can be assigned to C-H deformations of the aromatic ring [31]. The grape pomace hydroalcoholic extract is a complex matrix that may also contain organic acids, sugars, nitrogenous compounds, water and ethanol, but this work focused on flavonoids in the analysis of FT-IR spectra. This result indicates that grape pomace extracts contain flavonoids in their composition, which can act as corrosion inhibitors. The FT-IR spectra for A and B are almost the same, so it can be concluded that the extracts have the same composition, and differ mainly on their concentration.

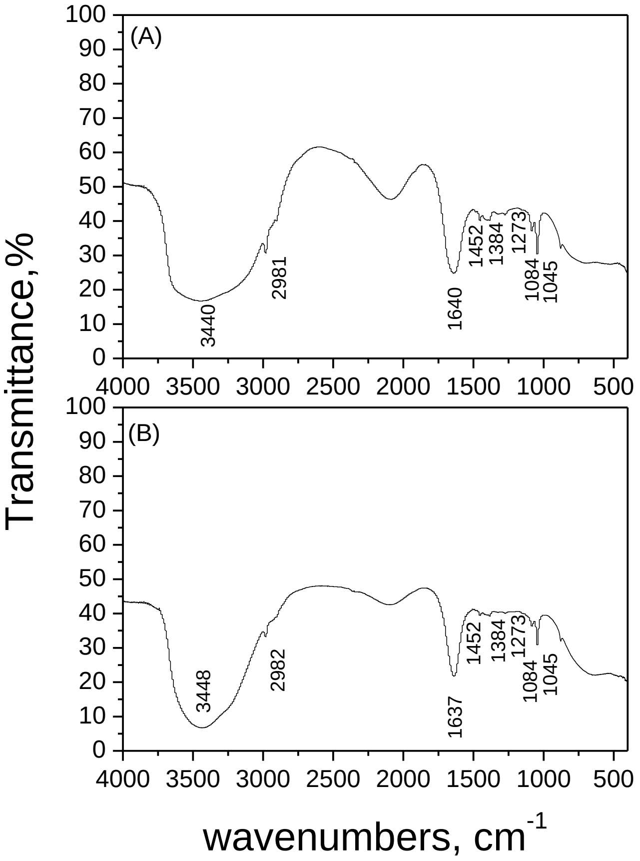

Figure 1. FT-IR spectra of crude (A) and concentrated (B) grape pomace extracts.

Contents of total phenolics and antioxidant activity of crude and concentrated grape pomace extracts are presented in Table 1. The concentrated grape pomace extract presented levels of total phenolics and antioxidant activity 6 and 5-fold higher than the crude extract, respectively. This result confirms that the grape pomace extracts present phenolic compounds, and that the concentration process was effective for these grape compounds. For instance, flavonoids are phenolic compounds that act as powerful antioxidants and form chelates with metals [35].

Table 1. Content of total phenolics and antioxidant activity for crude and concentrated grape pomace extracts.

Grape pomace extracts	Total phenolic (mg GAE/g)	Antioxidant activity (µmol TE/g)
Crude	110 ± 14.6	9.14 ± 1.12
Concentrated (8-fold by volume)	656 ± 63.1	49.6 ± 3.55

3.2. Potentiodynamic polarization curves

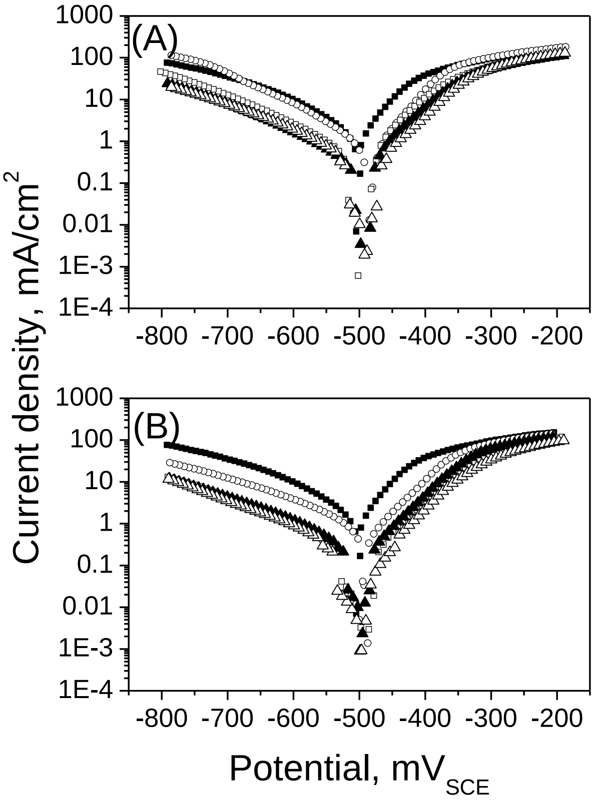

Figure 2. Polarization curves of C-steel in 1 mol L^{-1} HCl in the absence (■) and presence of crude (A) and concentrated (B) grape pomace extracts: 0.5% (○), 1% (□), 2% (▲), 3% (Δ).

Figures 2 (A-B) present the anodic and cathodic polarization curves of C-steel in 1 mol L^{-1} HCl solution in the absence and presence of crude and concentrated grape pomace extracts, respectively. From the potentiodynamic polarization curves, it can be seen that the corrosion potential remains almost constant in the presence of the extracts (data shown in Table 2). An inhibitor can be classified as cathodic or anodic if the difference in corrosion potential is more than 85 mV with respect to the corrosion potential of the blank [15]. Such results will indicate that the grape pomace extracts act as a mixed-type inhibitor. These results show that the grape pomace extracts can retard both anodic and cathodic reactions under open-circuit and polarised conditions.

The added extracts promoted a clear decrease in both anodic and cathodic current densities, probably due to adsorption of organic compounds from the extracts at the active sites of the electrode surface. This action might have hindered both metallic dissolution and hydrogen evolution reactions, and consequently slowing the corrosion process [14,15,19]. The decreased current densities were more pronounced with increases in inhibitor concentration, for both extracts.

3.3. Electrochemical impedance spectroscopy (EIS)

The Nyquist and Bode plots for C-steel in 1 mol L^{-1} HCl solution in the absence and presence of increasing extract concentrations of crude and concentrated grape pomace extracts are shown in Figures 3 and 4.

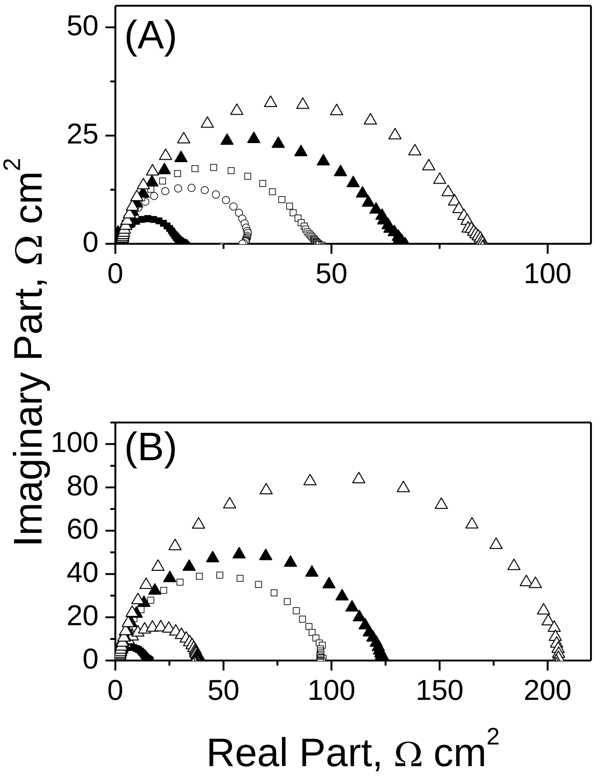

Figure 3. The Nyquist plots obtained at the corrosion potential for C-steel in 1 mol L^{-1} HCl solution in the absence (■) and presence of crude (A) and concentrated (B) grape pomace extracts: 0.5% (○), 1% (□), 2% (▲), 3% (Δ).

Impedance data is summarized in Table 2. The Nyquist diagrams, Figures 3 (A-B), show only one depressed capacitive loop, which is attributed to one time constant, in the absence and presence of the grape pomace extracts, which indicates two significant effects: the charge transfer resistance significantly increases and the f_{max} decreases in the presence of the extracts, decreasing the capacitance value, which may be caused by a reduction in the local dielectric constant and/or by an increase in the thickness of the electrical double layer [14]. These results show that the added extracts modified the electric double-layer structure, suggesting that the inhibitor molecules acted by adsorption at the metal/solution interface.

The solution resistance (Rs) is identical in the absence and presence of the grape pomace extracts and was approximately 1.5 Ω cm^2. Deviations from a perfect circular shape indicate frequency dispersion of interfacial impedance. This anomalous phenomenon is attributed in the literature to the heterogeneity of the electrode surface arising from the surface roughness or interfacial phenomena [36-37]. The charge-transfer resistance (R_{ct}) values were calculated from the difference in impedances at lower and higher frequencies. The double-layer capacitance (C_{dl}) was calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{3}$$

where f_{max} is the frequency at which the imaginary component of the impedance is maximal.

Table 2. Electrochemical parameters for C-steel in 1 mol L^{-1} HCl in the absence and presence of crude and concentrated grape pomace extracts

Medium	Inhibitor Concentration (%)	E_{corr} (mV)	R_{ct} (Ω cm^2)	f_{max} (Hz)	C_{dl} (μF cm^{-2})	I.E. (%)
Blank		-500	14.1	193	58.5	
Crude grape pomace						
	0.5	-481	29.1	62.5	87.5	52
	1	-490	45.7	47.1	73.9	69
	2	-490	64.9	47.1	52.1	78
	3	-489	83.5	47.1	40.5	83
Concentrated grape pomace						
	0.5	-492	37.2	62.5	68.5	62
	1	-489	94.2	35.6	47.5	85
	2	-496	122.7	26.8	48.4	88
	3	-491	203.2	20.2	38.8	93

A C_{dl} value of 58.5 μF cm^{-2} was found for the C-steel electrode in 1 mol L^{-1} HCl. From Table 2, it is clear that the R_{ct} values increased and that the C_{dl} values decreased with increasing inhibitor concentration. This result indicates a decrease in the active surface area caused by the adsorption of the inhibitors on the C-steel surface, and it suggests that the corrosion process became hindered. This hypothesis is corroborated by the anodic and cathodic polarization curve results. The inhibition efficiency increased as the extract concentration increased for both extracts. The best result for the inhibition efficiency of these extracts was obtained with a concentration of 3% for concentrated grape pomace extract with 93 % efficiency.

Figures 4 (A-B) present Bode plots of C-steel in 1 mol L^{-1} HCl solution in the absence and presence of both crude and concentrated grape pomace, respectively. From the curves, it can be seen that there is only one time constant, as in the Nyquist plots. The Bode plot of phase angle vs. log f shows a single peak at approximately 340 Hz, which remains constant with the addition of the extracts. The phase angle increased as the concentration of both extracts increased. For the modulus of the impedance the same trend was observed.

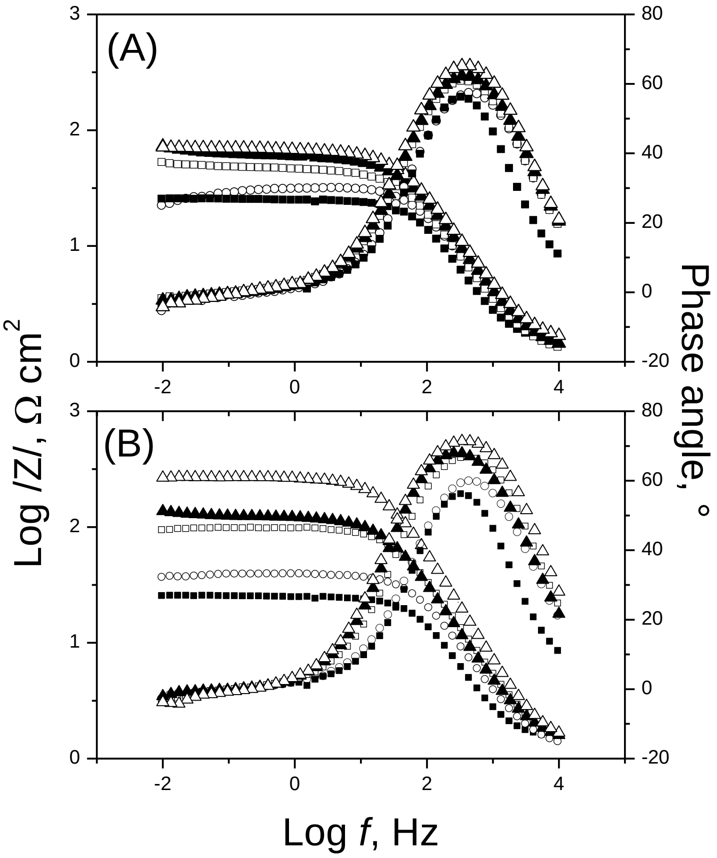

Figure 4. The Bode plots obtained at the corrosion potential for C-steel in 1 mol L^{-1} HCl solution in the absence (■) and presence of crude (A) and concentrated (B) grape pomace extracts: 0.5% (○), 1% (□), 2% (▲), 3% (Δ).

The interactions between the extracts and the C-steel surface can be examined by the adsorption isotherm. The inhibition efficiency is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ), which was calculated in this case using the equation θ = n/100. The adsorption isotherms most frequently used are Langmuir, Temkin, Frumkin and Flory-Huggins. Therefore, each of these adsorption isotherms was tested for its ability to describe the adsorption behavior of extracts on a C-steel surface in an HCl solution. The coefficient of determination (R^2) was considered to choose the isotherm that best fitted the experimental data. The linear relationships of *C/* θ vs. *C*, shown in Figure 5, suggest that the adsorption of grape pomace extracts on the C-steel obeyed the Langmuir adsorption isotherm. This isotherm can be represented as:

$$\frac{C}{\theta} = \frac{1}{K} + \mathrm{C} \qquad (4)$$

where C is the concentration of the extract and K is the adsorption constant.

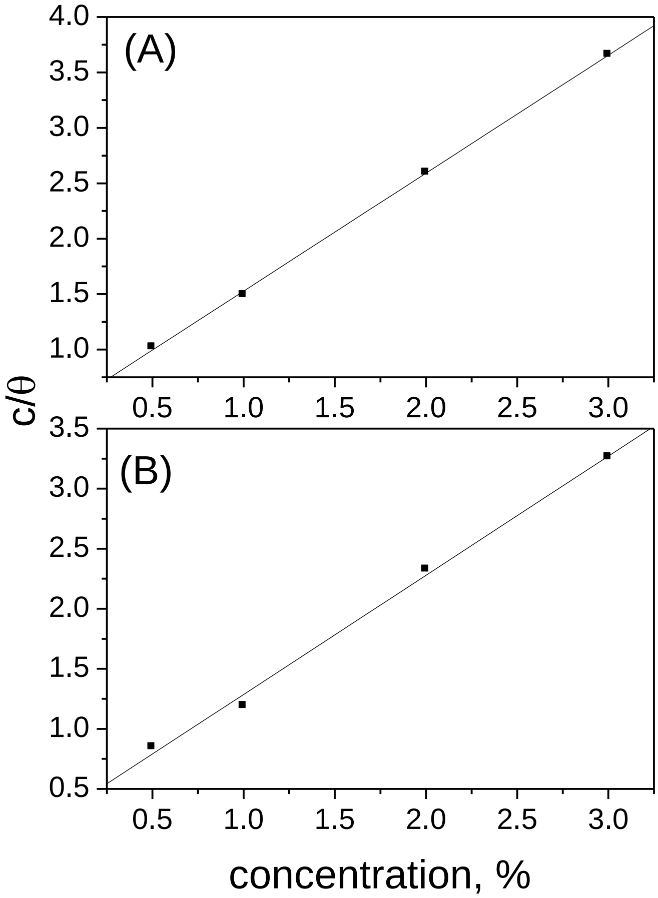

Figure 5. Langmuir adsorption isotherm of crude (A) and concentrated (B) grape pomace extracts.

Figure 5 depicts linear plots with high correlation coefficients of 0.9995 and 0.9959 and slopes of 1.0641 and 0.9921 for the crude and concentrated grape pomace extracts, respectively.

Because the molecular mass of the component responsible for the adsorption process is unknown, it is not possible to infer thermodynamic parameters, such as the standard free energy of adsorption value (ΔG_{ads}), from the adsorption isotherms. This limitation is common to studies using extracts of natural products as inhibitors, and was previously reported [14-15, 38-40].

3.4. Weight loss measurements

Results of weight loss measurements for C-steel in 1 mol L^{-1} HCl solution in the absence and presence of 2% of crude and concentrated grape pomace extracts, two immersion times (4 and 24 h) at 25 °C are presented in Table 3. These critical assays demonstrate the extracts stability in time. The C-steel corrosion rate (W_{corr}) was greatly reduced with the addition of grape pomace extracts for all immersion times. This behavior reflects the inhibitory effect of the extracts against C-steel corrosion in acid solution, corroborating the results obtained from electrochemical impedance diagrams and polarization curves. It is also noted that there was an increase in inhibition efficiency with time in the presence of crude and concentrated grape pomace extracts, from 84% after 4 h of immersion to 94% after 24 h for crude extract and from 95% to 97% for concentrated grape pomace extract. These results indicate that the inhibition efficiency was enhanced after longer periods of immersion.

Table 3. Data of C-steel weight loss in 1 mol L^{-1} HCl in the absence and presence of 2% crude and concentrated grape pomace extracts after 4 and 24 h of immersion at 25 °C.

Immersion time (hours)	Medium	W_{corr} (mg/cm^2 h)	Inhibition efficiency (%)
4	Blank	1.98	
	Crude grape pomace	0.33	84
	Concentrated grape pomace	0.09	95
24	Blank	1.74	
	Crude grape pomace	0.11	94
	Concentrated grape pomace	0.05	97

The apparent activation energy for the corrosion process was calculated from an Arrhenius-type plot according to the following equation [41]:

$$\log W_{corr} = \frac{-E_a}{2.303RT} + \log A \qquad (5)$$

where W_{corr} is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Arrhenius plots of (log W_{corr}) against ($1/T$) for C-steel in 1 mol L^{-1} HCl solution in the absence and presence of extracts are presented in Figure 6. The apparent activation energy obtained for the corrosion process was 51.5 kJ/mol and increased with the addition of crude and concentrated grape pomace extracts, to 91.8 kJ/mol and 97.5 kJ/mol, respectively. The value of E_a for C-steel corrosion in uninhibited 1 M HCl solution is on the same order of magnitude as literature data for steel in same acid solutions [42]. E_a values for the inhibited solutions are higher than that for the uninhibited one, indicating a strong inhibitive action for the studied compounds by increasing the energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the C-steel surface [43-45].

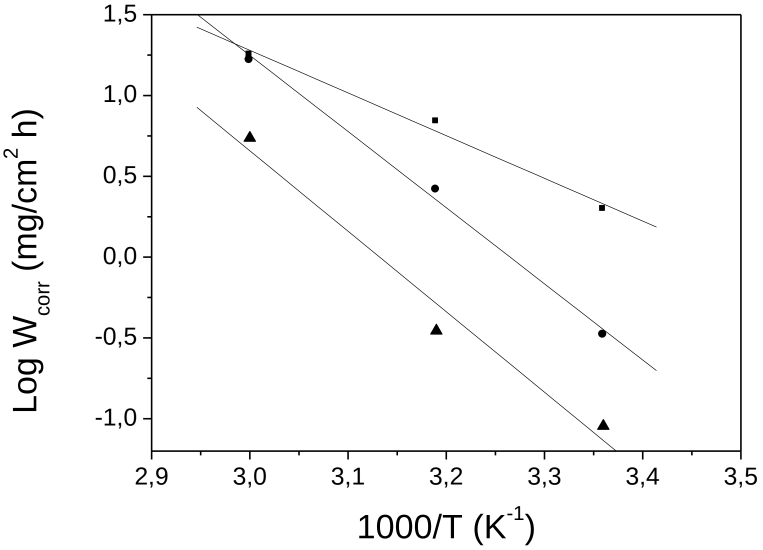

Figure 6. Arrhenius plots for the corrosion rate of C-steel in 1 mol L^{-1} HCl solution in the absence (■) and presence of 2% crude (●) and concentrated (▲) grape pomace extracts.

It was found that the corrosion rates of steel in both free and inhibited acid media increased as the temperature was increased (Table 4). Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency [46].

Table 4. C-steel weight loss data in 1 mol L^{-1} HCl in the absence and presence of 2% crude and concentrated grape pomace extracts, after 4 h of immersion, at 25, 40 and 60 °C.

Medium	Temperature							
	25 °C			40 °C			60 °C	
	W (mg/cm^2 h)	IE (%)		W (mg/cm^2 h)	IE (%)		W (mg/cm^2 h)	IE (%)
Blank	1.98	-		6.90	-		17.8	-
Crude grape pomace	0.33	84		2.61	62		16.5	7
Concentrated grape pomace	0.09	95		0.35	95		5.46	69

3.5. Surface analysis

Figure 7 shows an SEM micrograph recorded for C-steel samples polished (A) and exposed for 4 h in 1 mol L^{-1} HCl solution without (B) and with 2% crude (C) and concentrated (D) grape pomace extracts at 25 °C. The morphology in Fig. 7 B shows a rough surface, characteristic of the uniform corrosion of C-steel in acid without inhibitor, as previously reported [47]. In contrast, in the 1 mol L^{-1} HCl solution with added grape pomace extracts, a smooth surface was noticed (Figures 7 C-D). These results corroborate the electrochemical impedance analyses and weight loss measurement measurements, that C-steel corrosion was inhibited by the grape pomace extracts.

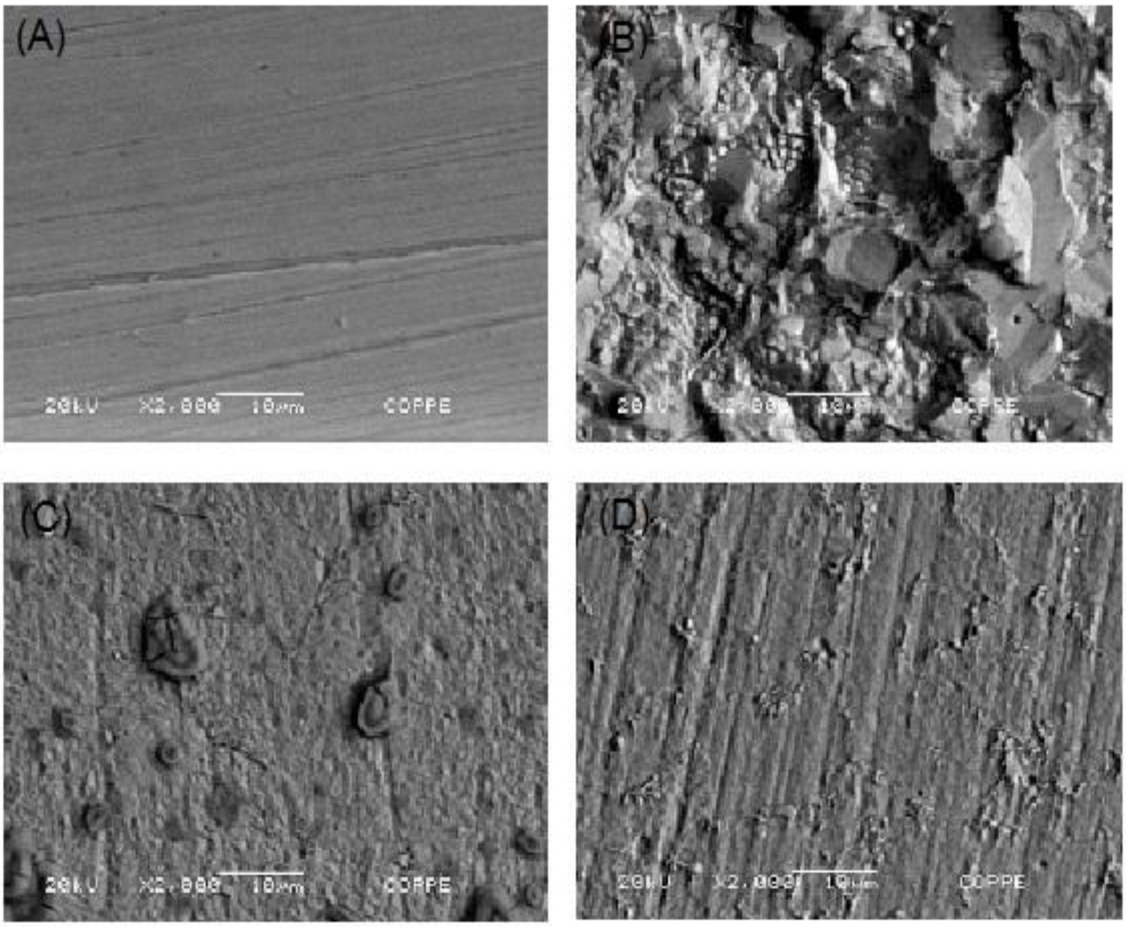

Figure 7. SEM photograph (x2,000) of C-steel: (A) polished surface, (B) C-steel immersed in 1 mol L^{-1} HCl and C-steel immersed in 1 mol L^{-1} HCl with 2% crude (C) and concentrated (D) grape pomace extracts.

3.6. Inhibition mechanism

The complex chemical compositions of these extracts make it rather difficult to attribute the inhibiting action to a particular component or group of components. The grape pomace is rich in polyphenolic compounds. Flavonoids are especially important antioxidants due to their high redox potential, which allows them to act as reducing agents, hydrogen donors, and singlet oxygen quenchers. In addition, they present metal chelation potential, forming specially bidentate metal chelates at the ortho-diphenolic groups of rings B and C (Figure 8) [48].

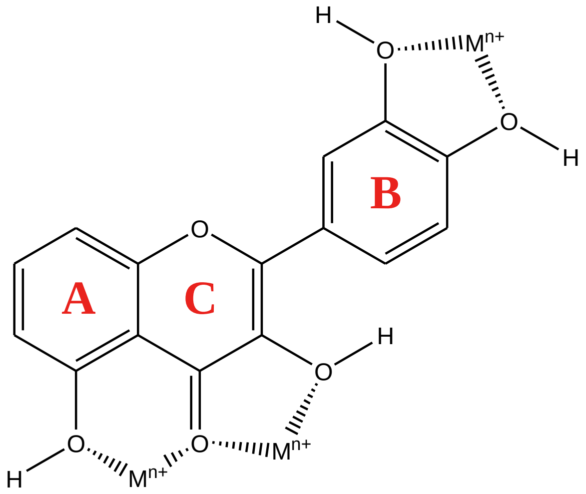

Figure 8. Theoretical binding sites in flavonoids for the chelation of transition metals.

Thus, it might be hypothesized that the inhibitory effect observed in polarization curves and electrochemical impedance diagrams probably occured via the adsorption of the flavonoids from the grape pomace extracts onto the steel surface.

4. CONCLUSIONS

Grape pomace extracts acted as corrosion inhibitors for C-steel in 1 mol L^{-1} HCl solutions. The inhibition efficiency of C-steel in 1 mol L^{-1} HCl increased with the concentration of crude and concentrated grape pomace extracts, and was inversely associated with temperature. Presumably, the inhibitory effect was performed via the adsorption of compounds present in the grape pomace extracts onto the steel surface. Flavonoids are good candidates to explain the corrosion inhibition effects observed for grape pomace extracts. The adsorption of the grape pomace extracts followed a Langmuir adsorption isotherm. The Ea of C-steel dissolution increased in presence of the grape pomace extracts. SEM revealed the persistence of a smooth surface on C-steel when grape pomace extracts were added, possibly due to the formation of an adsorptive film of phenolic compounds with electrostatic character.

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