Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution

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Abstract

The effects of aqueous extracts of spent coffee grounds on the corrosion of carbon steel in a 1 mol L⁻¹ HCl were examined. Two methods of extraction were studied: decoction and infusion. The inhibition efficiency of C-steel in 1 mol L⁻¹ HCl increased as the extract concentration and temperature increased. The coffee extracts acted as a mixed-type inhibitor with predominant cathodic effectiveness. In this study, the adsorption process of components of spent coffee grounds extracts obeyed the Langmuir adsorption isotherm. The chlorogenic acids isolated do not seem to explain the corrosion inhibition observed during the use of the coffee extracts.

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1. Introduction

Carbon steel is one of the most important alloys in existence and has a wide variety of industrial applications [1]. Acidic solutions are also commonly used throughout various industries, and applications include acid pickling, industrial cleaning, acid rascal- ing, oil-well acidification, and petrochemical processes. Because of the widespread applications of both carbon steel and acidic solutions, researchers have devoted attention to developing more-effective, non-toxic corrosion inhibitors to reduce the destructive effects of acids on metal surfaces [2]. Most inhibitors used in industry are organic compounds primarily composed of nitrogen, oxygen and sulphur atoms. Inhibitors containing multiple bonds play an important role in facilitating the adsorption of these compounds onto metal surfaces [3]. A bond can be formed between the electron pair and/or the π electron cloud of the donor atoms and the metal surface, thereby reducing corrosive attack in an acidic medium. Although there are many organic compounds with corrosion inhibiting properties described in the literature, the range of appropriate inhibitors for a particular system is very limited due to the specificity of the inhibitors and the great variety of systems in which corrosion can occur. Although many of these compounds have high inhibition efficiencies, many are undesirable due to their toxicity in humans, dangerous effects on the environment and high prices [1].

In recent years, research into the use of low-cost and eco-friendly compounds as corrosion inhibitors for mild steel has intensified [1,4–26]. Plant extracts are generally inexpensive and can be obtained through simple extraction processes. In addition, the development of technological uses for food residues may reduce the volume of waste discarded and increase the economic viability of appropriate waste management options.

The objective of this study was to investigate the inhibitory effects of aqueous coffee extracts as corrosion inhibitors for carbon steel in 1 mol L⁻¹ hydrochloric acid. The extracts were obtained from spent coffee grounds using two methods, decoction and infusion, to test the usability of the coffee residue. Open-circuit potential measurements, potentiodynamic polarisation curves, electrochemical impedance measurements and weight loss measurements were utilised.

2. Experimental

2.1. Inhibitor preparation

Aqueous extracts of spent coffee grounds were obtained using two methods: infusion and decoction. The type of coffee used in
our investigation is called Píão and is popular in Brazil. This commercial type of coffee is a blend of *Coffea arabic* and *Coffea canephora*, both of which are produced in São Paulo and in the Minas Gerais regions. In this study, commercial coffee (30 g) was used for conventional extraction in an electric coffee maker. A commercial paper filter and 300 mL of distilled water were used to prepare a coffee beverage in the typical fashion. The residue retained in the paper filter was dried in an oven at 50 °C for 24 h. After drying, the material was weighed (21.774 g) and divided into two 10 g aliquots for the following extraction procedures: (a) a 10-min decoction procedure in 100 mL of distilled boiling water and (b) a 30-min infusion procedure in 100 mL of distilled water with an initial temperature of 100 °C. Both extracts were filtered, lyophilized and stored at −4 °C until analysis. The lyophilized extracts of the spent coffee grounds were used as corrosion inhibitors for carbon steel in 1 mol L⁻¹ hydrochloric acid.

2.2. Phenolic components of the coffee extracts

The phenolic antioxidants of the coffee extracts were analysed using two methods: the colorimetric determination of total phenolics via reaction with the Folin–Ciocalteu reagent and an HPLC analysis of the chlorogenic acids. The analysis of the total phenolics in the aqueous coffee extracts was conducted essentially as described elsewhere [27]. Freeze-dried samples were extracted using acetone:water:acetic acid (70:29.5:0.5; v/v/v) and orbital shaking. Samples were reacted with the Folin–Ciocalteu reagent, the level of absorbance was read at 760 nm in a DU Beckman Spectophotometer (Beckman; CA, USA) and contents of the total phenolics were expressed as mg of gallic acid equivalents per gram of freeze–dried extract (mg GAE/g). Chlorogenic acids constitute the major phenolic components of roasted coffee and therefore were analysed as representative of the phenolic components of the samples. Chlorogenic acids were extracted from the freeze–dried samples as previously described [28]. The extracted samples were analysed using HPLC in a Shimadzu liquid chromatograph consisting of an LC-10AD vp quaternary pump and a SPD-M10A vp diode array detector. Five microlitres of each sample were injected through a Rhodyne valve into a Kromasil C18 HPLC column (150 × 4.6 mm, 5 μm, Eka Chemicals, NY, USA) and eluted using a solvent gradient. The HPLC solvent gradient, peak assignment, and quantitative analysis were used as previously described [29]. The results obtained are expressed in mg of chlorogenic acids per g of freeze–dried sample.

2.3. Electrochemical procedure

Working electrodes were prepared from steel specimens with the following composition (wt.%): C: 0.18, P: 0.04, S: 0.05, Mn: 0.30, Si: trace, and Fe: balance. The electrodes were prepared by embedding the steel rods in epoxy resin and exposing a surface area of 1 cm² to the electrolyte. Prior to each measurement, the sample surfaces were abraded with 400, 600 and 1000 grade emery paper, washed with double-distilled water, degreased with acetone and dried in warm air.

All electrochemical measurements were conducted in a thermostated conventional three-electrode Pyrex cell. A saturated calomel electrode (SCE) and a large-area platinum wire were used as the reference and auxiliary electrodes, respectively. The electrolyte was a 1 mol L⁻¹ HCl solution prepared from 37% HCl (pur- chased from Merck Co. (Darmstadt – Germany) and double distilled water. All experiments were carried out in 100 mL of non-stirred and naturally aerated electrolyte maintained at 25 °C.

In all experiments, the carbon steel electrode was allowed to reach its stable open-circuit potential (OCP), which occurred after 1 h. Electrochemical impedance measurements were performed over a frequency range of 100 kHz to 4 mHz at the stable open-circuit potential with an AC wave of 10 mV. The polarisation curves were also obtained after 1 h in the open-circuit potential. They ran from the cathodic to the anodic direction within the range of −850 to −250 mV/SCE with a scan rate of 1.0 mV s⁻¹.

The electrochemical experiments were performed using a PC-controlled VoltaLab 80 system with a PGZ2402 potentiostat (Radiometer Analytical) coupled with VoltaMaster 4 software.

The inhibition efficiency (n%) was calculated from potentiodynamic polarisation curves and electrochemical impedance diagrams as follows:

\[ n\% = \frac{j_{corr,0} - j_{corr}}{j_{corr,0}} \times 100, \]  

where \( j_{corr,0} \) is the density of the corrosion current in the absence of the inhibitor and \( j_{corr} \) is the density of the corrosion current in the presence of the inhibitor obtained from Tafel plots.

\[ n\% = \frac{R_{ct,0} - R_{ct}}{R_{ct,0}} \times 100, \]  

where is \( R_{ct,0} \) the charge-transfer resistance in the absence of the inhibitor and \( R_{ct} \) is the charge-transfer resistance in the presence of the inhibitor obtained from the electrochemical impedance diagrams.

2.4. Weight loss experiment

C-steel specimens with the same composition used in the electrochemical measurements were mechanically cut into 3.0 cm × 1.0 cm × 1.0 cm sections, polished with a silicon carbide emery cloth (grades 320, 400, 600 and 1000), washed with double distilled water, degreased with acetone and dried in warm air. Triplicate specimens were immersed in the acid test solutions in the absence and presence of 400 mg L⁻¹ aqueous extracts of used coffee grounds obtained by infusion for 24, 48 and 72 h at 25 °C. The temperature was controlled using an aqueous thermostat. Specimens were removed, rinsed in water and acetone, dried in warm air and stored in a desiccator. The weight loss was determined using an analytical balance with a precision of 0.1 mg. The inhibition efficiency (n%) was obtained using the equation

\[ n\% = \frac{W_0 - W}{W_0} \times 100, \]  

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

The effect of temperature on the corrosion rate for steel coupons in 1 mol L⁻¹ HCl solution at 25, 35, 45 and 55 °C was also examined. This experiment was performed in the absence and presence of 400 mg L⁻¹ aqueous coffee ground extracts obtained using the infusion process with an immersion period of 2 h.

In the present study, each experiment was repeated three times under the same conditions, and the relative differences between the replicate experiments were found to be smaller than 3%, indicating good reproducibility. The average of the three replicate values was used to further process the data.

2.5. Surface analysis

The specimens used to examine the surface morphology were immersed in 1 mol L⁻¹ HCl in the absence and presence of 400 mg L⁻¹ of aqueous coffee ground extracts obtained via decoc- tion and infusion at 25 °C for 2 h. The analysis was performed on a CARL ZEISS EVO MA-10 scanning electronic microscope. The accelerating voltage was 20 kV.
3. Results and discussion

3.1. Electrochemical experiments

3.1.1. Potentiodynamic polarisation curves

Fig. 1A and B present the potentiodynamic polarisation curves of C-steel in a 1 mol L\(^{-1}\) HCl solution in the absence and presence of aqueous coffee ground extracts obtained via decoction and infusion at 25 °C. The respective electrochemical parameters (i.e., corrosion potential (\(E_{corr}\)), corrosion current density (\(J_{corr}\)), and the anodic (\(\beta_a\)) and cathodic (\(\beta_c\)) Tafel constants, as shown in Table 1), were derived from Tafel plots.

From the potentiodynamic polarisation curves, it can be seen that the extracts caused a decrease in both anodic and cathodic current densities, most likely due to the adsorption of the organic compounds present in the extracts at the active sites of the electrode surface. This also slowed both metallic dissolution and hydrogen evolution and consequently slowed down the corrosion process. The two extracts exhibited the same behaviour.

![Polarisation curves for C-steel in 1 mol L\(^{-1}\) HCl in the absence and presence of aqueous coffee ground extract at various concentrations: 100, 200, 300 and 400 mg L\(^{-1}\). Extract obtained via decoction (A) and infusion (B).](image-url)

Table 1 indicates that, in the presence of the coffee extracts, both stable OCP and \(E_{corr}\) (derived from the Tafel plots) shifted cathodically with respect to the blank (7–34 mV and 10–28 mV, respectively). 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 [24]. Such results will indicate that the coffee extracts act as a mixed-type inhibitor with predominant cathodic effectiveness. These results show that the coffee extracts can retard both anodic and cathodic reactions under open-circuit and polarised conditions.

The corrosion current density (\(J_{corr}\)) decreased as the amount of the inhibitor increased, and this decrease was slightly more influential in the case of the extract obtained via infusion. The cathodic Tafel slopes (\(\beta_c\)) did not change significantly with the addition of the extracts (Table 1), indicating that the adsorbed inhibitor molecules do not affect hydrogen evolution; i.e., hydrogen evolution is diminished exclusively by the surface-blocking effect. The anodic region of the potentiodynamic polarisation curves can be seen as indicating an expressive increase in the anodic Tafel slopes (\(\beta_a\)) with the addition of the inhibitor. These results show that the adsorbed inhibitor to the carbon-steel modifies the metal dissolution process. The level of inhibition efficiency calculated based on the \(J_{corr}\) values obtained in the absence and presence of coffee extracts from decoction and infusion, respectively, falls between 78.7 and 83.5 and between 78.2 and 88.1 in the concentration range of 100–400 ppm.

3.1.2. Electrochemical impedance spectroscopy (EIS)

Fig. 2A–C illustrate the electrochemical impedance diagrams for C-steel in a 1 mol L\(^{-1}\) HCl solution in the absence and presence of aqueous extracts from coffee grounds. Table 2 summarises the impedance data from EIS experiments carried out in both the absence and the presence of increasing extract concentrations. In extract-free solutions, only one depressed capacitive loop was observed and that loop can be attributed to the time constant of the charge transfer and the double layer capacitance. Such a depression is characteristic of solid electrodes and is often ascribed to dispersion effects, which have been attributed to roughness and inhomogeneities on the surface during corrosion [18,21]. This behaviour is unaffected by the presence of the inhibitor, indicating the activation-controlled nature of the reaction during a one-charge transfer process. The intersection of this semicircle with the real axis at high frequencies produced a value of approximately 1.25 Ω cm\(^2\) for the ohmic resistance (\(R_0\)) of the solution. The charge-transfer resistance (\(R_{ct}\)) values were calculated based on the difference in impedance values at lower and higher frequencies. The double layer capacitance (\(C_{dl}\)) was calculated using the equation below:

\[
C_{dl} = \frac{1}{2\pi f_{max}R_{ct}},
\]

where \(f_{max}\) is the frequency at which the imaginary component of the impedance is maximal. A \(C_{dl}\) value of 475 μF cm\(^{-2}\) was determined for the C-steel electrode in 1 mol L\(^{-1}\) HCl. The electrochemical impedance diagrams obtained in the presence of the extract also show only one depressed capacitive loop. Based on Table 2, it is clear that the \(R_{ct}\) values increased and the \(C_{dl}\) values decreased with increasing inhibitor concentration. These results may be attributable to the adsorption of the components in the aqueous used coffee ground extracts onto the metal/solution interface. Indeed, this hypothesis is corroborated by the anodic and cathodic polarisation curves and the corrosion potential results. A comparison of the inhibition efficiencies obtained using the decoction and infusion methods shows that the values for the two methods are...
Table 1

Electrochemical parameters for C-steel in 1 mol L\(^{-1}\) HCl in the absence and presence of aqueous coffee ground extract at various concentrations: 100, 200, 300 and 400 mg L\(^{-1}\). Extracts were obtained via decoction and infusion.

<table>
<thead>
<tr>
<th>Medium</th>
<th>[Inhibitor] (mg L(^{-1}))</th>
<th>OCP (mV/SCE)</th>
<th>(E_{corr}) (mV/SCE)</th>
<th>(j_{max}) (mA cm(^{-2}))</th>
<th>(\beta_h) (mV/dec)</th>
<th>(-\beta_b) (mV/dec)</th>
<th>(n) (%)</th>
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</thead>
<tbody>
<tr>
<td>Blank</td>
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<td>-461</td>
<td>0.309</td>
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<td>101</td>
<td>-</td>
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<td>101</td>
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<td>200</td>
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<td>-489</td>
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<td>105</td>
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<td>-486</td>
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<td>108</td>
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<td>-489</td>
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<tr>
<td>BCINF extract</td>
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<td>-488</td>
<td>-487</td>
<td>0.0674</td>
<td>105</td>
<td>107</td>
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<td>-477</td>
<td>-483</td>
<td>0.0369</td>
<td>91</td>
<td>126</td>
<td>88.1</td>
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</tbody>
</table>

Table 2

Impedance data for C-steel in 1 mol L\(^{-1}\) HCl in the presence and absence of aqueous coffee ground extract at various concentrations: 100, 200, 300 and 400 mg L\(^{-1}\). Extracts were obtained via decoction and infusion.

<table>
<thead>
<tr>
<th>Medium</th>
<th>[Inhibitor] (mg L(^{-1}))</th>
<th>(R_{ct}) (Ω cm(^2))</th>
<th>(f_{max}) (Hz)</th>
<th>(C_{dl}) (μF cm(^{-2}))</th>
<th>(n) (%)</th>
</tr>
</thead>
<tbody>
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<td>Blank</td>
<td>-</td>
<td>10.6</td>
<td>31.6</td>
<td>475</td>
<td>-</td>
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<tr>
<td>BCINF extract</td>
<td>100</td>
<td>69</td>
<td>40.0</td>
<td>58</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>90</td>
<td>31.6</td>
<td>56</td>
<td>88</td>
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<td>93</td>
</tr>
<tr>
<td>BCINF extract</td>
<td>100</td>
<td>87</td>
<td>40.0</td>
<td>46</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>107</td>
<td>31.6</td>
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<td></td>
<td>400</td>
<td>198</td>
<td>20.0</td>
<td>40</td>
<td>95</td>
</tr>
</tbody>
</table>

The variation in \(\theta\) according to the extract concentration indicates the adsorption isotherm that describes the system. The fit to the Langmuir isotherm was determined by plotting \(C/\theta\) versus \(C\) according to the following equation:

\[
\frac{C}{\theta} = \frac{1}{K + C},
\]

where \(K\) is the adsorption equilibrium constant. Fig. 3 displays linear plots with high correlation coefficients of 0.9997 and 0.9998 and a slope of 1.034 and 1.024 for the decoction and infusion extracts, respectively. This behaviour suggests that the compounds present in the coffee ground extracts adsorbed onto the C-steel surface were consistent with a Langmuir adsorption isotherm, indicating the absence of interaction forces between the adsorbed molecules. The decoction and infusion extracts behaved similarly; the values of the adsorptive equilibrium constants at 25 °C are 0.0571 and 0.0645 L mg\(^{-1}\). It is important to emphasise that some authors have compared the adsorptive equilibrium constant values obtained from natural product extracts with those of good acid inhibitors such as Tween-85 (0.9608 L mg\(^{-1}\) for \(K\)) but that such a comparative analysis is inappropriate if the molecular mass of the components responsible for the adsorption process is unknown [19]. Therefore, it is also impossible to discuss the behaviour of adsorption isotherms supporting the use of natural product extracts as inhibitors in terms of thermodynamic parameters, such as the standard free energy of adsorption value (\(\Delta G_{\text{ads}}\)) [18], if the chemical nature of the adsorbed substance is unknown. Unfortunately, the literature has employed this incorrect approach [21].
3.2 Weight loss measurements

The results of the weight loss measurements associated with the corrosion of C-steel in a 1 mol L⁻¹ HCl solution in the absence and presence of 400 mg L⁻¹ aqueous coffee ground extracts obtained via infusion for varying periods of time (24, 48 and 72 h) at 25 °C are provided in Table 3. These assays were critical in determining the stability of the extract with time. It was observed that the rate of C-steel corrosion significantly decreased upon the addition of coffee ground extracts for all immersion times. These results indicate the inhibitory effect of this extract on C-steel corrosion in acidic solution. It is also clear that inhibition efficiency decreases with time, as it dropped from 97% after 24 h of immersion to 80% after 72 h. There was some deterioration of the protective layer formed in the presence of the aqueous coffee ground extracts on the C-steel surface. These results are important because the immersion times normally used in the literature are much lower than those tested in the experiments presented here. The data also indicate that inhibition efficiency can remain relatively high with long periods of immersion.

The effect of temperature on the corrosion of C-steel in a 1 mol L⁻¹ HCl solution ranging from 25 to 55 °C with 2 h of immersion time is presented in Table 4. The experiments were performed in the absence and presence of 400 mg L⁻¹ aqueous coffee ground extracts obtained by infusion. The corrosion rates for steel in both free and inhibited acid media increased as the temperature increased. Additionally, the inhibition efficiency of the coffee grounds extract increased with temperature.

The apparent activation energy associated with C-steel corrosion in free and inhibited acid solution was determined using an Arrhenius-type plot according to the following equation:

$$\log W_{corr} = \frac{-E_a}{2.303RT} + \log A,$$

where $W_{corr}$ is the corrosion rate, $E_a$ is the apparent activation energy, $A$ is the frequency factor, $T$ is the absolute temperature and $R$ is the molar gas constant. Arrhenius plots of $(\log W_{corr})$ against $(1/T)$ for C-steel in a 1 mol L⁻¹ HCl solution in the absence and presence of the coffee ground extracts are shown graphically in Fig. 4. The apparent activation energy obtained for the corrosion process in the free acid solution was found to be 41.9 kJ/mol and 16.8 kJ/mol in the presence of the inhibitor.
barrier of the corrosion reaction decreased in the presence of the inhibitor. The inhibition efficiency level also increased as the temperature increased (Table 4). Bouyanzer et al. have traced such observations to specific interactions between the steel surface and the inhibitor \cite{17,30}. The lower value of $E_a$ in the corrosion process in the presence of inhibitor, as compared to that in a free acid solution, can be attributed to the chemisorption of the inhibitor on the steel surface.

3.3. Phenolic components of the coffee extracts

Phenolic compounds and alkaloids are substances normally found in coffee samples \cite{31} and are generally considered to be the main corrosion inhibitors present in extracts of natural products \cite{23,26}. It emerged that the amount of phenolics overall and the amounts of individual chlorogenic acids were slightly higher (approximately 15–20\%) in the extract obtained via the infusion of spent coffee grounds than in the extract obtained using decoction (Table 5). Although it could be expected that decoction would be a more effective method of extracting water-soluble compounds, exposure to a temperature of 100 $^\circ$C during decoction may have resulted in the degradation of the compounds investigated and therefore in higher levels of antioxidant components in the infusion extract. These higher levels of phenolic compounds in the infusion extract might in turn explain the slightly higher degree of corrosion inhibition observed for the infusion extract (Tables 1 and 2). In contrast, the aqueous extracts of spent coffee grounds were found to be similar in terms of their relative distribution of chlorogenic acids. These results are consistent with all of the electrochemical analyses, which revealed relatively similar behaviour. Free caffeic acid was not detected in either type of spent coffee extract.

Table 5

<table>
<thead>
<tr>
<th>Phenolic components</th>
<th>Coffee extracts</th>
<th>BC INF extract</th>
<th>BC INF extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-CQA (mg/g)</td>
<td>10.5</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>5-CQA (mg/g)</td>
<td>14.4</td>
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</tr>
<tr>
<td>3-FQA (mg/g)</td>
<td>3.3</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>4-CQA (mg/g)</td>
<td>11.4</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>5-FQA (mg/g)</td>
<td>1.7</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>4-FQA (mg/g)</td>
<td>1.3</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>3,4-diCQA (mg/g)</td>
<td>3.4</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>3,5-diCQA (mg/g)</td>
<td>2.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>4,5-diCQA (mg/g)</td>
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<td>2.0</td>
<td></td>
</tr>
<tr>
<td>CFQA (mg/g)</td>
<td>2.0</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>CGA (mg/g)</td>
<td>51.3</td>
<td>74.9</td>
<td></td>
</tr>
<tr>
<td>Total phenolics (mg GAE/g)</td>
<td>64.2</td>
<td>77.2</td>
<td></td>
</tr>
</tbody>
</table>

3-CQA: 3-caffeoylquinic acid; 5-CQA: 5-caffeoylquinic acid; 3-FQA: 3-feruloylquinic acid; 4-CQA: 4-caffeoylquinic acid; 5-FQA: 5-feruloylquinic acid; 4-FQA: 4-feruloylquinic acid; 3,4-diCQA: 3,4-dicaffeoylquinic acid; 3,5-diCQA: 3,5-dicaffeoylquinic acid; 4,5-diCQA: 4,5-dicaffeoylquinic acid; CFQA: Total caffeoylferuloylquinic acids; CGA: Total chlorogenic acids.

![Chemical structure of 5-caffeoylquinic acid.](image)

**Fig. 5.** Chemical structure of 5-caffeoylquinic acid.

3.4. Studies with isolated 5-caffeoylquinic acid

Isolated 5-caffeoylquinic acid, as indicated in Fig. 5, was studied using electrochemical impedance in 1 mol L$^{-1}$ HCl because it is the major chlorogenic acid that was found in both of the extracts. The corresponding results are presented in Fig. 6 and Table 6. Again, the electrochemical impedance diagrams obtained using the chlorogenic acid show only one depressed capacitive loop with a slight increase in charge transfer resistance. Table 6 lists a selection of electrochemical parameters for C-steel in 1 mol L$^{-1}$ HCl in the absence and presence of the standard. The stable open-circuit potential was slightly more negative when chlorogenic acid was used. The inhibition efficiency levels of the chlorogenic acid were 28% and 33% in the presence of 100 and 200 mg L$^{-1}$, respectively. These values of inhibition efficiency are several times lower than those observed for the coffee extracts (Tables 1 and 2). It should be noted that, although the concentration levels of the total chlorogenic

![Impedance diagrams for C-steel in a 1 mol L$^{-1}$ HCl solution in the absence and presence of 5-caffeoylquinic acid (5-CQA).](image)

**Fig. 6.** Impedance diagrams for C-steel in a 1 mol L$^{-1}$ HCl solution in the absence and presence of 5-caffeoylquinic acid (5-CQA).
acids (CGA, Table 5) during the electrochemical analyses of the coffee extracts were relatively low, varying from 7.5 to 30 and 5.1 to 21 ppm, respectively, in the assays of infused and decocted coffee extracts, the corrosion inhibition efficiency was approximately 90% for all coffee extracts. Thus, it would seem that isolated chlorogenic acids do not seem to be responsible for the corrosion inhibition results observed for the coffee extracts. In the present study, it is not possible to determine what components present in the coffee extracts created their relatively high ability to inhibit corrosion. However, it can be speculated that other components present in the coffee extracts might have precipitated the observed effects and that a complex synergistic relationship between chlorogenic acids and other components of coffee may have been responsible for the results of this study.

### 3.5. Surface analysis

Fig. 7 shows a SEM photograph recorded for C-steel samples immersed for 2 h in a 1 mol L$^{-1}$ HCl solution in the absence (A) and presence of 400 mg L$^{-1}$ of aqueous coffee grounds extracts obtained using decoction (B) and infusion (C) at 25 °C. The morphology in Fig. 7A shows the type of rough surface characteristic of the uniform corrosion of C-steel in acid as previously reported [18], indicating that in extract-free solution, the surface is highly corroded. C-steel immersed in 1 mol L$^{-1}$ solution with either type of coffee extract was noted to have a smooth surface (Fig. 7B and C), indicating that the surface was protected by the extracts. These results corroborate all of the electrochemical and weight loss measurements.

### 4. Conclusions

Aqueous extracts of coffee grounds can act as an effective, naturally derived, green corrosion inhibitor for C-steel in a 1 mol L$^{-1}$ HCl solution.

1. All electrochemical results, including the slightly more negative values for OCP and corrosion potential, the indications of inhibitory action in the anodic and cathodic polarization curves and the electrochemical impedance measurements, showed that the examined extracts acted as mixed-type inhibitors with predominant cathodic effectiveness.

2. The adsorption of the studied extracts was consistent with the Langmuir adsorption isotherm.

3. The inhibition efficiency of C-steel in 1 mol L$^{-1}$ HCl increased with the temperature increases.

4. The apparent activation energy ($E_a$) of C-steel dissolution decreased when the extract was used.

5. The action of the extract as a corrosion inhibitor for C-steel in acid solution can be attributed to a strong chemisorptive bond.

6. The slight differences between the coffee extracts in terms of chlorogenic acid composition and total phenolic contents are consistent with the slight differences observed between the two extracts in terms of inhibitory efficiency.

7. The presence of isolated chlorogenic acids does not seem to explain the corrosion inhibition observed for the coffee extracts. In the present study, it is impossible to determine what components present in the coffee extracts caused their relatively high ability to inhibit corrosion.

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References