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# Barley Agro-industrial Residues as Corrosion Inhibitor for Mild Steel in 1mol $L^{-1}$ HCl Solution

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The corrosion inhibition of mild steel in 1 mol $L^{-1}$HCl by barley grains and malting process residue extracts was investigated by weight loss measurements, polarization curves, electrochemical impedance measurements and scanning electron microscopy. The inhibition efficiency exceeded 92% in the presence of 100 mg $L^{-1}$ extracts after 24 h immersion time for both extracts. The $E_a$ decreased with the addition of the extracts, characterizing the chemical adsorption by the molecules present in the extracts on the surface.The high molecular weight fraction isolated from the barley grain extract also showed high inhibition efficiency, suggesting that macromolecules are probably responsible for the inhibitory action.

**Keywords:** *Inhibitor, Acid Corrosion, EIS, Polarization, Weight Loss Measurements.*

## 1. Introduction

The use of inhibitors is one of the best methods for corrosion protection of metals, especially in acidic media. Most well-known acid inhibitors are organic compounds containing nitrogen (N-heterocyclic), sulfur, long carbon chain or aromatic and oxygen atoms[1].

The various hazardous effects of most synthetic corrosion inhibitors have motivated the use of safe natural products. They can provide a renewable source of naturally available chemical compounds that can be extracted by simple extraction and at low cost[2].

Agro-industrial activities produce thousands of tons of wastes all over the world. Many of these wastes are harnessed as animal feed or arranged on own field[3]. These wastes have great quantities of nutrients and antioxidant compounds, which could be used to obtain chemical formulations with inhibitory activity towards corrosion[4].

Recently, interest has increased with the development and use of low-cost and eco-friendly compounds as corrosion inhibitors[1-2,5-33]. In our previous works, the effect of aqueous extracts of spent coffee grounds, coffee husk, garlic, and onion peels, fruit peels (mango, orange, passion fruit and cashew), grape pomace and papaya seeds on the corrosion of carbon steel in 1 mol $L^{-1}$HCl was studied[9-15].

The most commonly used grain for the production of beer is malting barley, and the initial stage of the manufacturing process includes the production of barley malt. The process of malting barley (*Hordeum vulgare L.*) includes the following main steps: a) cleaning and storage of the grains, b) immersion of the grains in water and subsequent germination, and c) transformation of the green malt (the product of germination) into dry malt. The malting process is an enzymatic conversion of starch into maltose[34]. In the malting process, the residual material is the barley which has not germinated, i.e., it floated in the water and it will not be able to become malt.

Barley is an excellent source of β-glucans, phenolic compounds, acid ascorbic, glutathione, and several amino acids as alanine, glycine, serine, leucine, valine, tyrosine, and isoleucine, which could be able to adsorb onto the metallic surface[2].

M. Saadawy reported the use of the barley extract as a friendly inhibitor for the steel corrosion in 0.5 mol $L^{-1}$ $H_2SO_4$[2]. The extract was obtained by refluxing 10 g of the sample powder in 100 mL of water for 1 h. According to the author, the barley extract acted as an effective corrosion inhibitor for the acid corrosion of steel, reaching 94% of inhibition efficiency in the presence of 0.84 g $L^{-1}$ barley extract. The inhibiting action of the barley extract was attributed to its adsorption onto the metal surface blocking both anodic and cathodic sites. Adsorption isotherms indicated that the adsorbed molecules cover one active center on the metal surface. In addition, the inhibition efficiency decreases as

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the temperature increases, showing an inhibition associated with physical adsorption.

The objective of this work is to investigate the inhibitory action of malting process residues, as well as barley grain extracts on the corrosion of mild steel in HCl solution by weight loss measurements, open circuit potential (OCP) measurements, potentiodynamic polarization curves (PPC) and electrochemical impedance spectroscopy (EIS), as well as through surface analysis using scanning electron microscopy (SEM).

## 2. Experimental

### *2.1 Obtaining the extracts*

Barley grains and malting process residue were used as corrosion inhibitors, which were supplied by a Brazilian Agroindustrial Cooperative. 20.0 g of crushed material was placed in 200 mL of double-distilled water previously boiled for infusion for 1 hour. Next, the filtration was performed and the filtrate was stored in glass containers and placed in a freezer at −4 ºC.

The vessels containing the frozen filtrate were placed in a lyophilizer the Liotop brand, model L101 at −52 ºC so that all the water contained in the sample was removed without its structure modified, generating a powder as a final product.

In order to elucidate the inhibitory action by these extracts, the high molecular weight fraction (HMWF) from the aqueous barley grains was also used as a corrosion inhibitor. This fraction was obtained using an ultrafiltration method where a 100 mL aliquot of the barley grain extract was added to an ultrafiltration apparatus with 3 kDa cutoff (Millipore, USA) which was immediately centrifuged. The fraction retained by the membrane was washed three times with double distilled water and then lyophilized and stored at −4 ºC before analysis.

### *2.2 Test solution*

An electrolyte of 1mol $L^{-1}$ HCl was prepared from 37% m/v HCl (Merck Co., Darmstadt-Germany) and double distilled water. All experiments were carried out in 100 mL electrolyte under non-stirred and naturally aerated conditions.

### *2.3 Electrochemical Techniques*

#### *2.3.1 Weight-loss measurements*

Mild steel specimens with the following composition (wt.%): C: 0.18, P: 0.04, S: 0.05, Mn: 0.30, Si: trace and Fe: balance were abraded with 100-grade emery paper, sandblasted, washed with double-distilled water, degreased with acetone, and dried in air. Weight loss was determined by gravimetric tests using an analytical balance with a precision of 0.1 mg.

In trials varying time, three mild steel coupons were placed in glass containers so that the entire surface was in contact with 1 mol $L^{-1}$ HCl solution. The solutions in the absence and presence of the inhibitor at concentrations ranging: 100, 200, 400 and 1000 mg $L^{-1}$ were poured into containers and allowed the intervals of 2, 6 and 24 h. After the elapsed time, the coupons were removed from the solutions, rinsed with double distilled water and acetone, dried and weighed again.

Each essay contained three coupons and the inhibition efficiency was obtained by the average of the three replicated values. Inhibition efficiency (*IE*%) was calculated from the equation 1[35]:

$$IE\% = \left[\left(W_{corr,0} - W_{corr}\right)/W_{corr,0}\right] \mathrm{x}\, 100 \quad (1)$$

Where $W_{corr}$ and $W_{corr,0}$ are the mild steel corrosion rates in 1 mol $L^{-1}$ HCl, in the presence and absence of the extract, respectively, in g $cm^{-2}$ $h^{-1}$.

The tests with temperature variation were performed at 25, 35, 45 and 55 ºC for 4 h in the presence and absence of 400 mg $L^{-1}$ of the extract. The temperature was controlled using an aqueous thermostat. After the elapsed time, the coupons were removed from the solutions, rinsed with double distilled water and acetone, dried and weighed again.

In the present study, each experiment was repeated three times under the same conditions, and the relative differences between replicate experiments were found to be low according to the standard deviation presented. The average of the three replicated values was used for further processing of the data.

#### *2.3.2 Open circuit potential measurements*

OCP, PPC and EIS measurements were conducted in a conventional three-electrode Pyrex cell which was composed by a mild steel coupon as the working electrode, a saturated calomel electrode ($Hg/Hg_2Cl_2/Cl^-$) as the reference electrode and a platinum wire as the counter electrode.

In these cases, mild steel coupons were abraded using polishing machine AROPOL 2V (AROTEC) and water emery paper with a granulometry of 100, 320, 600 and 1200 mesh, washed with double-distilled water and dried.

The electrochemical measurements were performed using an AUTOLAB - PGSTAT 128 N potentiostat/galvanostat, controlled by GPES 4.9 electrochemical software from Eco-Chemie (The Netherlands).

For all electrochemical analyzes, the potential of the open circuit was monitored in 4000 seconds until it became constant.

#### *2.3.3 Potentiodynamic polarization curves*

Anodic and cathodic polarization curves were obtained in the absence and presence of the extract, varying the potential from −300 mV to +300 mV relative to the open circuit potential at a speed of 1 mV $s^{-1}$.

After obtaining the polarization curves, the Tafel extrapolation method was used, where the corrosion current densities, $j_{corr}$, were obtained and *IE*% values were calculated according to equation 2[35].

$$IE\% = \left[ \left( j_{corr,0} - j_{corr} \right) / j_{corr,0} \right] \text{x } 100 \qquad (2)$$

Where $j_{corr,0}$ and $j_{corr}$ are the mild steel corrosion current densities in 1 mol $L^{-1}$HCl media in the absence and presence of the inhibitor, respectively.

### *2.3.4 Electrochemical impedance spectroscopy*

This test was performed using the FRA software where the impedance measurements were performed by applying 10 mV (rms) as a disturbance in a frequency range from 100 kHz to 10 mHz, with a working electrode at the stable open circuit potential.

Using this technique, the electrochemical parameters such as the charge transfer resistance ($R_{ct}$) were determined. With this value assigned, it is possible to calculate the degree of surface coverage ($\theta$) and the inhibition efficiency, *IE*%, which are given by equations 3 and 4[35], respectively:

$$IE\% = \left( R_{ct} - R_{ct,0} \right) / R_{ct} \qquad (3)$$

$$IE\% = \left[ \left( R_{ct} - R_{ct,0} \right) / R_{ct} \right] \text{x } 100 \qquad (4)$$

Where $R_{ct,0}$ and $R_{ct}$ are the mild steel charge transfer resistances in 1 mol $L^{-1}$ HCl media in the absence and presence of the inhibitor, respectively.

### *2.4 Scanning Electron Microscopy (SEM)*

In order to analyze the morphology of the mild steel surface, two coupons were mechanically abraded with 100 to 2000-mesh emery papers, as described in the electrochemical assays. After abrading, the specimens were washed with double distilled-water, degreased with acetone and finally dried.

Each coupon was immersed in 1 mol $L^{-1}$ HCl solution for 2 hours in the absence and presence of 400 mg $L^{-1}$ extract; thereafter, they were taken out of the solution and washed with double distilled water, degreased with acetone and dried.

After this procedure, the coupons were analyzed through a scanning electron microscope JEOL JSM 6460LV with an acceleration voltage of 20kV.

### *2.5 Total Phenolic Content*

The total phenol was quantified using the method used by Singleton *et al.*, by the reaction of the sample with the Folin reactant and the calibration curve of Gallic acid[36].

200 µL of Gallic acid standard solution (from 10 to 130 mg $L^{-1}$) and 2500 mg $L^{-1}$ of each extract were added to a test tube in which 1400 µL of Mili-Q water and 100 µL of Folin reactant were also added. The tube containing the solution and the sample was stirred on a vortex, and then waited for a minimum of 30 seconds and a maximum of 8 minutes, and 300 µL of a 20% $Na_2CO_3$ solution (m/v) was added. The tube was placed in a water bath at 40ºC for 30 minutes.

The absorbance of the solution and the sample containing the extract was measured using a spectrophotometer, model Lambda XLS, Perkin Elmer brand, at a wavelength of 765 nm.

## 3. Results and Discussion

### *3.1 Weight-loss Measurements*

The results of the gravimetric assays for the mild steel varying time and extract concentration are shown in Table 1.

As it can be seen in Table 1, higher immersion times lead to lower corrosion rates ($W_{corr}$) and consequently higher inhibition efficiencies for all the extracts, indicating they are all stable. The increase in inhibition efficiency with increasing immersion time is due to the increase in the surface coverage with time. These results also reveal that the adsorption of the extracts on the mild steel is relatively long.The increase in the efficiencies with the extract concentration increase demonstrates that the surface coverage by the inhibitory molecules present in the extracts increases. This result can be attributed to the increase in the number of molecules occupied by the inhibitor at the metal interface.

Both studied extracts are efficient corrosion inhibitors, and the greatest efficiencies were obtained for a concentration of 1000 mg $L^{-1}$ for 24 h immersion time, being 95.7% for barley grain extract and 94.5% for malting process residue. Therefore, the malting process residue extract has inhibition efficiency as high as the barley grains and can be used as corrosion inhibitors for mild steel in HCl solution.

Table 2 shows the results obtained from the weight loss measurements performed for 4 hours of total immersion of the mild steel, in the absence and presence of 400 mg $L^{-1}$ of the extracts at different temperatures, varying from 25 to 55 ºC.

The results indicate an increase of the corrosion rates in the absence and presence of the inhibitors as the temperature increases, growing more in its absence, leading to an increase in the inhibition efficiency with the temperature. Figure 1 shows the Arrhenius graph for mild steel in 1 mol $L^{-1}$ HCl media, in the absence and presence of 400 mg $L^{-1}$ of the extracts. The apparent activation energies were calculated (Table 3) from the Arrhenius plots equation (5)[37,38], which represent the relationship between ln $W_{corr}$ and the reciprocal of the absolute temperature.

$$\ln W_{corr} = \ln A - \left( E_a / \mathrm{R}T \right) \qquad (5)$$

Where A is the frequency factor, $E_a$ is the apparent activation energy, R is the constant for ideal gases and $T$ is the absolute temperature.

**Table 1.** Weight loss measurements varying time and inhibitor concentration.

| time (h) | [extract] (mg $L^{-1}$) | Barley Grain | | | Malting process residue | | |
|---|---|---|---|---|---|---|---|
| | | $W_{corr}$ | SD | *IE%* | $W_{corr}$ | SD | *IE%* |
| | | (g $cm^{-2}h^{-1}$) | | | (g $cm^{-2}h^{-1}$) | | |
| **2** | **0** | $1.97x10^{-3}$ | $1.5x10^{-4}$ | - | $2.32x10^{-3}$ | $6.9x10^{-5}$ | - |
| | **100** | $5.08x10^{-4}$ | $3.0x10^{-5}$ | 74.2 | $6.47x10^{-4}$ | $2.6x10^{-5}$ | 72.1 |
| | **200** | $4.22x10^{-4}$ | $1.7x10^{-5}$ | 78.6 | $5.67x10^{-4}$ | $3.3x10^{-5}$ | 75.6 |
| | **400** | $3.50x10^{-4}$ | $2.9x10^{-5}$ | 82.2 | $5.14x10^{-4}$ | $1.4x10^{-5}$ | 77.8 |
| | **1000** | $2.63x10^{-4}$ | $2.8x10^{-5}$ | 86.6 | $4.05x10^{-4}$ | $2.3x10^{-5}$ | 82.5 |
| **6** | **0** | $1.89x10^{-3}$ | $9.9x10^{-5}$ | - | $1.92x10^{-3}$ | $1.1x10^{-4}$ | - |
| | **100** | $3.77x10^{-4}$ | $4.6x10^{-6}$ | 80.1 | $4.06x10^{-4}$ | $2.8x10^{-5}$ | 78.9 |
| | **200** | $2.85x10^{-4}$ | $8.4x10^{-6}$ | 84.9 | $3.27x10^{-4}$ | $2.0x10^{-5}$ | 83.0 |
| | **400** | $2.48x10^{-4}$ | $1.1x10^{-6}$ | 86.9 | $2.97x10^{-4}$ | $2.0x10^{-5}$ | 84.5 |
| | **1000** | $2.15x10^{-4}$ | $7.6x10^{-6}$ | 88.6 | $2.63x10^{-4}$ | $1.1x10^{-6}$ | 86.3 |
| **24** | **0** | $1.76x10^{-3}$ | $1.4x10^{-4}$ | - | $1.6x10^{-3}$ | $1.0x10^{-4}$ | - |
| | **100** | $1.20x10^{-4}$ | $1.6x10^{-5}$ | 93.2 | $1.3x10^{-4}$ | $2.1x10^{-5}$ | 91.7 |
| | **200** | $9.99x10^{-5}$ | $1.8x10^{-5}$ | 94.3 | $1.1x10^{-4}$ | $5.9x10^{-6}$ | 93.1 |
| | **400** | $8.77x10^{-5}$ | $1.5x10^{-5}$ | 95.0 | $9.5x10^{-5}$ | $6.7x10^{-6}$ | 94.0 |
| | **1000** | $7.50x10^{-5}$ | $9.7x10^{-6}$ | 95.7 | $8.8x10^{-5}$ | $4.3x10^{-6}$ | 94.5 |

SD: standard deviation

**Table 2.** Weight loss measurements varying temperature in the absence and presence of 400 mg $L^{-1}$ of the inhibitor after 4 h immersion time.

| T (ºC) | Blank | | Inhibitor | | |
|---|---|---|---|---|---|
| | $W_{corr}$ | SD | $W_{corr}$ | SD | *IE %* |
| | (g $cm^{-2}h^{-1}$) | | (g $cm^{-2}h^{-1}$) | | |
| | **Barley grain** | | | | |
| **25** | $2.96x10^{-3}$ | $7.1x10^{-5}$ | $8.45x10^{-4}$ | $2.7x10^{-5}$ | 71.5 |
| **35** | $4.62x10^{-3}$ | $1.9x10^{-5}$ | $8.48x10^{-4}$ | $1.9x10^{-5}$ | 81.6 |
| **45** | $7.12x10^{-3}$ | $2.0x10^{-4}$ | $1.02x10^{-3}$ | $7.9x10^{-5}$ | 85.7 |
| **55** | $1.07x10^{-2}$ | $3.3x10^{-4}$ | $1.31x10^{-3}$ | $8.7x10^{-5}$ | 87.8 |
| | **Malting process residue** | | | | |
| **25** | $2.86x10^{-3}$ | $1.9x10^{-4}$ | $5.47x10^{-4}$ | $7.6x10^{-5}$ | 80.9 |
| **35** | $4.48x10^{-3}$ | $7.8x10^{-5}$ | $8.03x10^{-4}$ | $1.9x10^{-5}$ | 82.1 |
| **45** | $7.15x10^{-3}$ | $2.7x10^{-4}$ | $1.17x10^{-3}$ | $2.5x10^{-5}$ | 83.6 |
| **55** | $1.07x10^{-2}$ | $2.3x10^{-4}$ | $1.61x10^{-3}$ | $3.9x10^{-5}$ | 85.0 |

SD: standard deviation

There is a decrease in the apparent activation energy in the presence of the extracts when compared to the blank assay. It may indicate that there is a chemical adsorption between the extract molecules and the mild steel surface. This behavior is different from that one presented by M. Saadawy where the *IE* decreased with the temperature increase, showing a physical interaction between the barley extract and the steel surface[2]. It is important to remember that the methodology used by M. Saadawy to obtain the extract was different from this work. In Saadawy's work, the extract was obtained by refluxing 10 g of the powder sample in 100 mL of water for 1 hour and the sample was not specified by the author. In addition, it was not clear if the sample used of barley was grain or another part of it. Another important point is the studied medium, in the present work it is the HCl solution and in Saadawy'swork it was $H_2SO_4$, perhaps showing the role of the anion in the adsorption process.

An alternative formulation of Arrhenius equation is[37,38]:

$$W_{corr} = RT/Nh \exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \quad (6)$$

Where h is Planck's constant, N is Avogadro's number, $\Delta S^*$ is the entropy of activation and $\Delta H^*$ is the enthalpy of activation. A plot of $\ln(W_{corr}/T)$ vs. $1/T$ gave a straight line with a slope of $\Delta H^*/R$ and an intercept of $\ln(R/Nh)+\Delta S^*/R$ (Figure 2), from which the values of $\Delta S^*$ and $\Delta H^*$ were calculated

and listed in Table 3. The data in Table 3 reveal the values of the thermodynamic activation functions ($E_a$ and $\Delta H^*$) for corrosion of the mild steel in 1 mol $L^{-1}$ HCl solution in the absence and presence of the inhibitor. A lower value of $E_a$ and $\Delta H^*$ in the presence of the inhibitor were observed. This phenomenon could be attributed to the chemisorption of the inhibitor involving charge transfer from the molecules of the barley grain and malting process residue extracts to the mild steel surface. This conclusion is corroborated by the increase in inhibition efficiency with increasing temperature. The positive signs of enthalpies $\Delta H^*$ obtained reflect the endothermic nature of the dissolution process[39].

The values of $E_a$ are larger than the analogous values of $\Delta H^*$, indicating that the corrosion process must involve a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume. Moreover, the value of the difference $E_a - \Delta H^*$ is 2.6 kJ $mol^{-1}$, which is equal to the average value of RT (2.6 kJ $mol^{-1}$) and indicates that the corrosion process is a unimolecular reaction[40]. The entropy of activation $\Delta S^*$ was negative both in the absence and presence of the inhibitor, which implies that the activated complex represents the rate-determining step with respect to the association instead of the dissociation step. This implies that there was a decrease in the disorder when going from the reactants to the activated complex.

Again, the behavior presented by the barley grain extract has also been seen by the malting process residue, showing that the inhibition mechanism should be the same for both extracts.

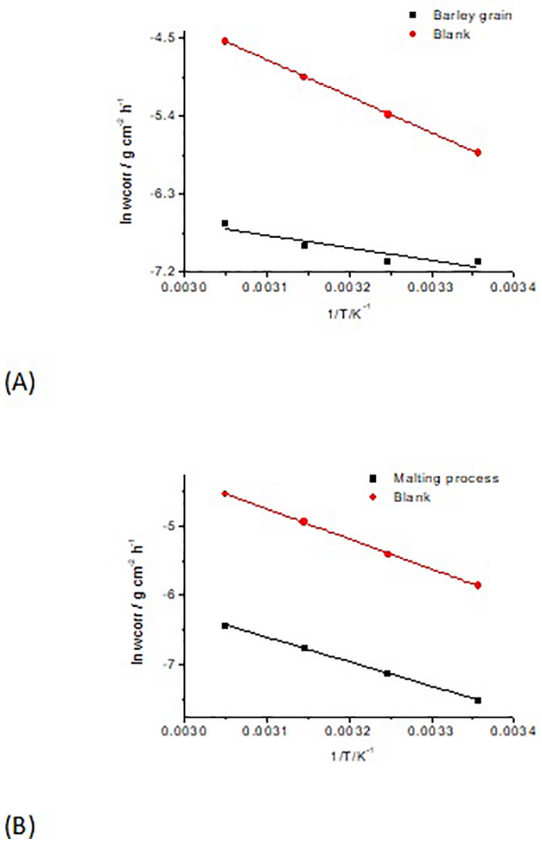


**Figure 1.** Arrhenius plots ln $W_{corr}$ x 1 /$T$: (A) Barley grain and (B) Malting process residue; for mild steel in 1 mol $L^{-1}$HCl in the absence and presence of the extracts.

## 3.2 Electrochemical Assays

### 3.2.1 Electrochemical impedance

Figure 3 shows the electrochemical impedance diagrams obtained in the open circuit potential of the mild steel in 1 mol $L^{-1}$HCl medium, in the absence and presence of different concentrations of the studied extracts. In the inhibitor-free solutions, only one depressed capacitive loop was observed which can be related to a single time constant attributed to the charge transfer and the double layer capacitance.Such depressions are characteristic of solid electrodes and are commonly referred to as dispersion effects due to surface roughness and inhomogeneities during corrosion[41].

In addition, it can be observed that the electrochemical impedance diagrams obtained in the presence of the extracts show two depressed capacitive loops. The first capacitive loop is due to electrical double layer relaxation and the second one that appears in the lower frequency range,which can be attributed to an intermediary species relaxation involving the inhibitory molecule and consequently to the inhibitory film. A significant effect can be observed: the charge transfer resistance, $R_{ct}$, which corresponds to the first capacitive loop diameter and whose value is the measurement of the transfer of electrons across the surface and is inversely proportional to the corrosion rate, increases significantly with the increase in extract concentration[41].

In inhibitor-free solutions, the electrochemical impedance diagram was analyzed based on the equivalent circuit shown in Figure 4A, where $R_s$ represents the ohmic resistance of the solution, $R_1$ represents the resistance to charge transfer ($R_{ct}$) and $CPE_1$ is the constant phase element, which was used instead of a double layer capacitor to give a more precise adjustment.

**Table 3.** Activation parameters ($E_a$, $\Delta H^*$ and $\Delta S^*$) for mild steel corrosion in the absence and presence of 400 mg $L^{-1}$ of the different extracts.

| | $E_a$(kJ $mol^{-1}$) | | $\Delta H^*$(kJ $mol^{-1}$) | | $\Delta S^*$(J $K^{-1}mol^{-1}$) | |
|---|---|---|---|---|---|---|
| | **Blank** | **Inhibitor** | **Blank** | **Inhibitor** | **Blank** | **Inhibitor** |
| **Barleygrain** | 34.9 | 12.0 | 32.3 | 9.39 | -185 | -273 |
| **Malting Process residue** | 36.0 | 29.3 | 33.4 | 26.7 | -182 | -218 |

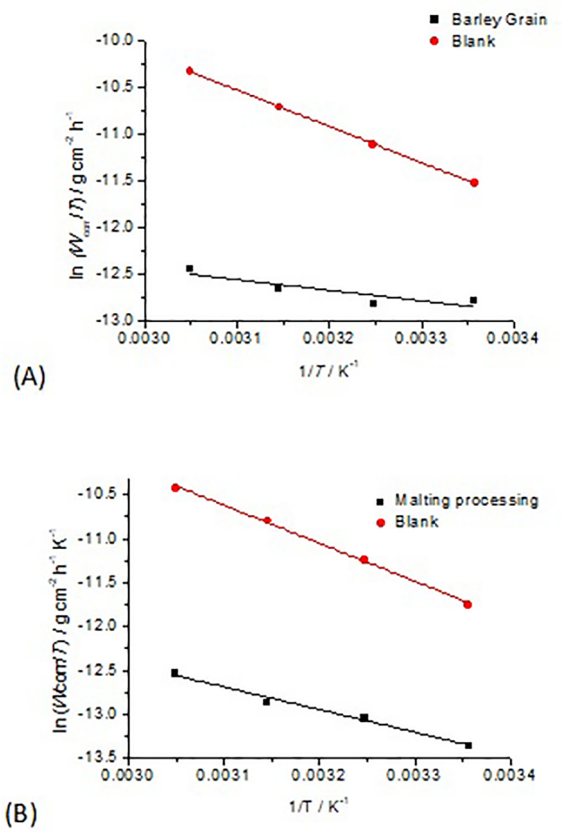


**Figure 2.** Arrhenius plots ln ($W_{corr}/T$) x 1/$T$for mild steel in 1 mol $L^{-1}$HCl in the absence and presence of the extracts: (A) Barley grainand (B) Malting process residue.

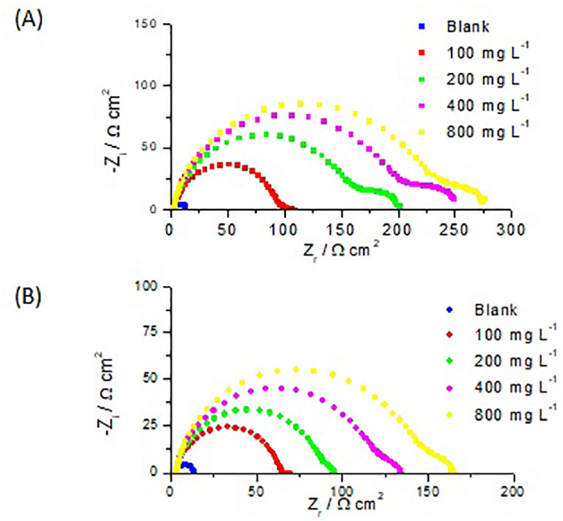


**Figure 3.** Electrochemical impedance diagrams for mild steel in 1 mol $L^{-1}$ HCl media in the absence and presence of different extract concentrations; A: Barley grain and B: malting process residue.

For fitting the EIS results in inhibitor containing solutions, the electrochemical equivalent circuit was modified and is shown in Figure 4B. In this circuit, $CPE_2$ element represents the adsorption capacitance, which corresponds to the inhibitor-

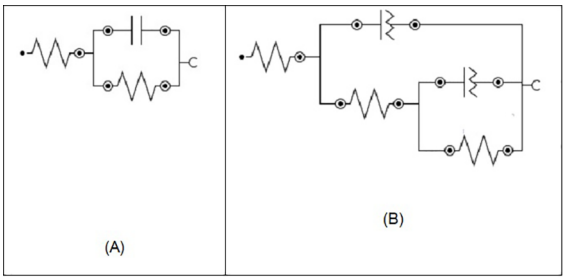


**Figure 4.** Equivalent circuits used to fit the obtained impedance spectra for mild steel in the absence (A) and presence of the inhibitors (B).

adsorbed surface, and $R_2$ is the resistance corresponding to the second loop, which corresponds to the resistance of the inhibitory film formed on the metal surface.

Table 4 shows the parameters obtained by adjusting the recorded EIS data using the equivalent circuits of Figure 4A and 4B. The increase in the extract concentration increases the charge transfer resistance ($R_{ct}$). The $R_{ct}$values showed that both extracts are a very effective inhibitor in the HCl solution, reaching 91.8 and 89.8% *IE* for 800 mg $L^{-1}$ extracts of barley grain and malting process residue, respectively. Once again, the malting process residue extract shows inhibition efficiencies as high as the barley grains.

The adsorption of an organic adsorbate between the metal/solution interface can be considered as a replacement adsorption process between the organic molecules in the aqueous solution $Org_{(soln)}$ and the water molecules on the metal surface $H_2O_{(ads)}$[31,42].

$$Org_{(soln)} + xH_2O_{(ads)} \longrightarrow Org_{(ads)} + xH_2O_{soln} \quad (7)$$

Where $Org_{(ads)}$ are the organic molecules adsorbed on the metal surface, $H_2O_{(soln)}$are the water molecules in the aqueous solution and x is the size ratio representing the number of water molecules replaced by an organic adsorbate molecule.

From the electrochemical impedance data, it was possible to determine the degree of coverage of the metal surface (Θ) as a function of inhibitor concentration. The experimental results were adjusted to different adsorption isotherms (Langmuir, Temkin, Flory-Huggins and El-Awady) according to equations[31,39-40]:

$$\text{Langmuir: } C/\Theta = 1/K + C \quad (8)$$

$$\text{Temkim: } \Theta = (-2.303/2a)\log K + (-2.303/2a)\log C \quad (9)$$

$$\text{Flory} - \text{Huggins: } \log(\Theta/C) = \log K + x\log(1-\Theta) \quad (10)$$

$$\text{El} - \text{Awady: } \log(\Theta/(1-\Theta)) = \log K + y\log C \quad (11)$$

**Table 4.** Electrochemical parameters obtained from the electrochemical impedance spectroscopy.

| [Inh] (mg $mL^{-1}$) | $R_1$ ($\Omega cm^2$) | $n_1$ | $CPE_1$ ($\mu F\ cm^{-2}$) | $Y0_1$ ($\mu Mhocm^{-2}$) | $R_2$ ($\Omega\ cm^2$) | $n_2$ | $CPE_2$ ($\mu F\ cm^{-2}$) | $Y0_2$ ($\mu Mhocm^{-2}$) | IE% |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Barley Grain** | | | | | |
| **Blank** | 13.3 | 0.89 | 136 | 269 | - | - | - | - | - |
| **100** | 92.6 | 0.85 | 58.1 | 126 | - | - | - | - | 85.6 |
| **200** | 154 | 0.85 | 33.8 | **73.5** | 47.1 | 0.64 | 13.0 | 16.9 | 91.4 |
| **400** | 185 | 0.86 | 32.2 | 63.9 | **77.3** | 0.48 | 13.7 | 12.4 | 92.8 |
| **800** | 162 | 0.88 | 28.4 | 52.5 | 134 | **0.30** | **1.28** | 3.52 | 91.8 |
| | | | | **Malting process residue** | | | | | |
| **Blank** | 13.3 | 0.89 | 136 | 269 | - | - | - | - | - |
| **100** | 62.0 | 0.87 | 60.8 | 127 | - | - | - | - | 78.5 |
| **200** | 85.6 | 0.86 | 42.7 | 94.1 | 6.56 | 0.86 | 25.2 | 36.3 | 84.4 |
| **400** | 114 | 0.86 | 35.1 | 74.4 | 16.9 | 0.72 | 7.63 | 15.7 | 88.3 |
| **800** | 131 | 0.88 | 30.5 | 59.4 | 3.33 | 0.54 | 3.33 | 8.80 | 89.8 |

Langmuir's theory admits that adsorption occurs at a specific and homogeneous site and each inhibitory molecule holds only one site[31].

The Temkin isotherm assumes that the heat of adsorption of all the molecules covering the adsorbent decreases linearly as a function of the coating due to the interactions between the adsorbed molecules (a> 0, attraction, <0, repulsion)[31].

The Flory-Huggins isotherm believes that an active site may be occupied by more than one inhibitory molecule (parameter x). X greater than one unit indicates that more than one molecule of $H_2O_{(ads)}$ was substituted by an organic molecule, ie, x is the number of water molecules replaced by an inhibitory molecule[31].

Awady *et al.*consider that a single inhibitory molecule can adsorb more than one active site (parameter y)[43]. Y smaller than one unit shows that a single inhibitory molecule was adsorbed on more than one active site, ie, y is the number of inhibitory molecules occupying an active site on the metal surface[43].

The Langmuir isotherm showed a better linear regression coefficient values, with a coefficient of determination ($r^2$) of 0.9997 and 0.9999 and an angular coefficient of 1.08 and 1.08, for extracts of barley grain and malting process residue, respectively (Figure 5 and Table 5). This behavior suggests that the molecules present in these extracts were adsorbed onto the mild steel surface according to a Langmuir adsorption isotherm, which accepts that the inhibition is produced by monolayer adsorption on the metal surface containing a fixed number of adsorption sites, and each site holds an adsorbate with no interaction between the adsorbate molecules. As the angular coefficient is greater than one, this can be considered as a Langmuir isotherm deviation, the existence of interactions between the adsorbed molecules and/or a number other than one of inhibitory molecules occupying an active site can be considered[31].

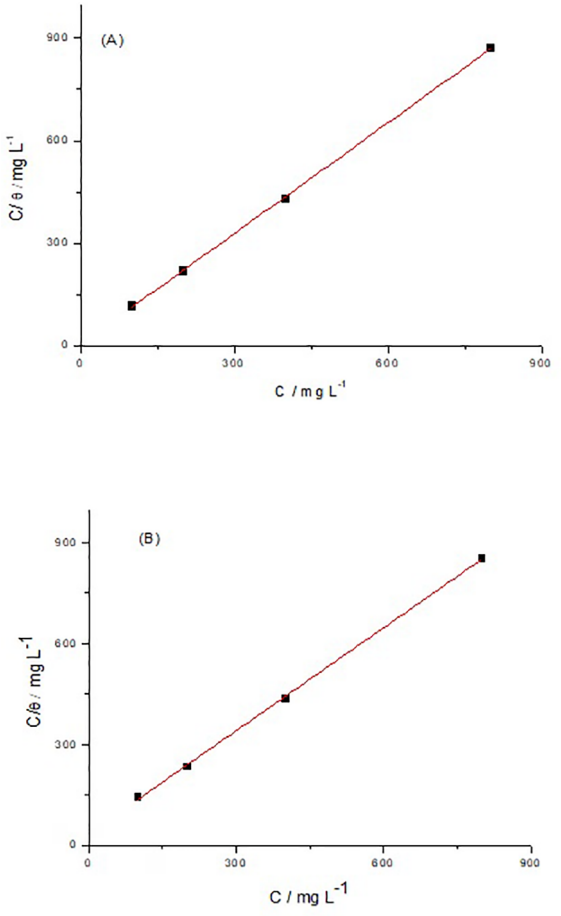


**Figure 5.** Langmuir adsorption isotherm of A: Barley grain and B: malting process residue extracts on the mild steel in 1.0 mol $L^{-1}$HCl.

From the Temkin isotherm it is possible to admit that there is a repulsive interaction between the inhibitory molecules adsorbed, once a <0. It is also possible to consider that more than one molecule of $H_2O_{(ads)}$ was substituted by an inhibitor

**Table 5.** Langmuir, Temkin, Flory-Huggins and El Awady Isotherms parameters.

| Inhibitor | Isotherm parameters | Langmuir | Temkin | Flory-Huggins | El Awady |
|---|---|---|---|---|---|
| **Barley Grain** | $r^2$ | 0.9997 | 0.6318 | 0.6028 | 0.6282 |
| | Angular coeficient | 1.08 | 0.0661 | 2.217 | 0.3008 |
| **Malting process residue** | $r^2$ | 0.9999 | 0.9364 | 0.9661 | 0.9675 |
| | Angular coeficient | 1.08 | 0.1255 | 2.484 | 0.4297 |

molecule once for the Flory-Huggins equation x> 1 and for the El-Awady equation y <0.

In summary, the angular coefficient obtained from the Langmuir isotherm makes it appear that the relationship between the active site and the adsorbed molecule is not a unit. This fact seems to be confirmed by the Flory-Huggins and El-Awady isotherms; a single inhibitory molecule is adsorbed on more than one active site where there was one molecule of water.

These results suggest the existence of a monolayer on the mild steel surface, which involves the chemical adsorption of bulky molecules on the metallic surface. Since the chemical nature of the adsorbed molecules is unknown, the determination of the thermodynamic parameters such as $\Delta G^0$ is not possible[9-16,31].

### *3.2.2 Potentiodynamic polarization curves*

Figure 6 shows the anodic and cathodic curves for the mild steel in 1 mol $L^{-1}$HCl solution, obtained in the absence and presence of the studied extracts.

The presence of the extract reduced the anodic and cathodic current densities, and this effect is more pronounced in the cathodic branch, indicating that these extracts act as a mixed inhibitor with a cathodic character predominating.

Table 6 shows the electrochemical parameters such as corrosion potential ($E_{corr}$), corrosion current density ($j_{corr}$) and anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes obtained by the Tafel extrapolation method and the open-circuit potential (*OCP*).

For all extracts, the open circuit potential (*OCP*) showed a small anodic displacement with respect to the blank with a maximum displacement of 10 and 23 mV in the presence of barley grains and malting process residue extracts, respectively. The corrosion potential ($E_{corr}$), derived from the Tafel plots, exhibited a cathodic shift with respect to the blank with a maximum displacement of 39 and 42 mV for $E_{corr}$ in the presence of barley grains and malting process residue extracts, respectively. These results suggest that under open circuit condition the extracts retard both anodic and cathodic reactions, demonstrating that all extracts act as a mixed type inhibitor with a predominant anodic character. However, when the working electrode is polarized, this behavior changes, shifting the $E_{corr}$ to more negative values

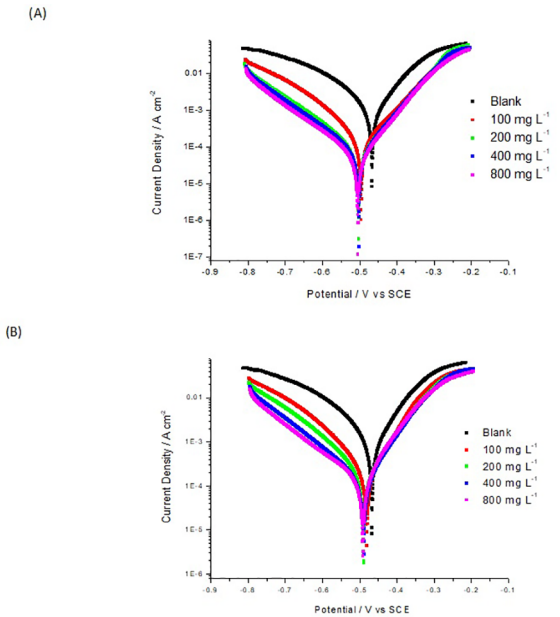


**Figure 6.** Polarization curves for mild steel in 1 mol $L^{-1}$ HCl in the absence and presence of different extract concentrations; A: Barley grain andB: malting process residue.

with respect to the blank test, showing that the inhibitory molecule adsorption depends on the applied potential being more pronounced in cathodic polarization.

As can be seen in Table 6, there were no significant changes in the values of the anodic and cathodic Tafel slopes, both for the anodic ($\beta_a$) and cathodic curves ($\beta_c$), indicating that the inhibitor does not change the mechanisms of the anodic and cathodic processes, responsible for the dissolution of the metal and the reduction of hydrogen, respectively. These results would suggest that these inhibitors could be purely blocking type acting just by surface screening, however, the impedance diagrams results showed a second capacitive loop at the open circuit potential, concluding that these extracts could change the corrosion mechanism.

The presence of the extract decreased the corrosion current density ($j_{corr}$) in the presence of the inhibitor relative to the blank test. The greatest efficiencies were obtained for a concentration of 800 mg $L^{-1}$, being 93.8% for barley grain extract, and 84.0% for the malting process residue. These

**Table 6.** Electrochemical parameters obtained from polarization curves.

| Inhibitor (mg $L^{-1}$) | *OCP* (mV) | $E_{corr}$ (mV) | $\beta_a$ (mV $dec^{-1}$) | $-\beta c$ (mV $dec^{-1}$) | $j_{corr}$ (mA $cm^{-2}$) | *IE%* |
|---|---|---|---|---|---|---|
| | | | **Barley grain** | | | |
| **Blank** | −515 | −455 | 71.6 | 122 | 8.26 x$10^{-1}$ | |
| **100** | −507 | −476 | 92.6 | 136 | 1.67 x$10^{-1}$ | 79.8 |
| **200** | −509 | −491 | 84.1 | 139 | 7.20 x$10^{-2}$ | 91.3 |
| **400** | −505 | −494 | 83.6 | 142 | 6.65 x$10^{-2}$ | 91.9 |
| **800** | −506 | −494 | 79.5 | 145 | 5.08 x$10^{-2}$ | 93.8 |
| | | | **Malting process residue** | | | |
| **Blank** | −515 | −455 | 71.6 | 122 | 8.26 x$10^{-1}$ | |
| **100** | −498 | −461 | 73.9 | 147 | 2.62 x$10^{-1}$ | 68.3 |
| **200** | −492 | −482 | 87.1 | 136 | 1.78 x$10^{-1}$ | 78.5 |
| **400** | −495 | −487 | 85.2 | 150 | 1.34 x$10^{-1}$ | 83.8 |
| **800** | −495 | −497 | 88.5 | 160 | 1.32 x$10^{-1}$ | 84.0 |

results confirm the results obtained by electrochemical impedance.

### *3.3 Surface analysis*

Figure 7 shows an SEM micrograph of mild steel immersed for 2 h in 1 mol $L^{-1}$HCl in the absence (Fig. 7a) and presence of 400 mg $L^{-1}$ of the extracts of barley grain (Fig. 7b) and malting process residue(Fig. 6c) at room temperature. The morphology in Fig. 7a shows a rough surface, characteristic of the uniform corrosion of mild steel in acid. In the presence of the extracts (Fig. 7b and 7c), a smooth surface can be observed, indicating that the surface was protected by the inhibitor. These results are in agreement with the electrochemical experiments and weight loss measurements and demonstrate a protective mild steel inhibitor when immersed in a 1 mol $L^{-1}$HCl solution containing all extracts: barley grain and malting process residue.

### *3.4 Total phenols test*

The extracts of barley grain and malting process residue presented 88.4 and 377 mg GAE/100 g sample, respectively. For the barley grain, the total phenol content is in agreement with the value registered by Bezerra for barley grains from 75.25 to 156.4 mg/100 g sample[44].

These results show that the total phenol content cannot be solely responsible for the corrosion inhibition of mild steel. The *IE* obtained from the gravimetric and electrochemical results of these extracts was quite identical, but the malt processing residue extract had a total phenolic content four times higher than the barley grain extract.

In our previous work, it was shown that the total phenolic content of the extracts does not correlate with their inhibition efficiencies[16,45].

## 4. Mechanism

The complex chemical compositions of the extracts make it rather difficult to attribute the inhibitory action to a particular constituent or group of constituents.

According to the literature, the barley grain presents an elongated shape and it is made of a more resistant outer layer, the shell. Besides, it presents three subsequent layers, the pericarp, the forehead and the aleurone layer. Most of the grain is occupied by the endosperm, where the reserve substances of the plant could be found. The main chemical compounds of barley grain are cellulose, pentosans, phenolic compounds, silica, lipids, sugars, proteins, enzymes, vitamin B, minerals, beta-glucans, starch[46].

The infusion, extraction procedure used in this work, will extract the more polar substances such as proteins, phenolic compounds, vitamin B, starch, sugars. Thus, the inhibitory effect observed in the polarization curves, electrochemical impedance diagrams,and weight loss measurements is likely to occur via the adsorption of some of these substances present in the barley extracts on the steel surface. It was seen that the total phenol content does not correlate with the inhibition efficiency of the extracts. Macromolecules such as starch and proteins are soluble in water and could be responsible for the inhibitory action of the barley extracts.

Based on this, in the present study, the high molecular weight fraction (HMWF), rich in macromolecules such as proteins and/or polysaccharides, was isolated from the aqueous barley grain extract. This fraction was also studied by weight loss measurements for 2 h immersion varying inhibitor concentration and temperature and by electrochemical assays of impedance and polarization curves in 1 mol $L^{-1}$HCl. In weight loss measurements, the inhibition efficiency of HMWF obtained after 2 h of immersion time

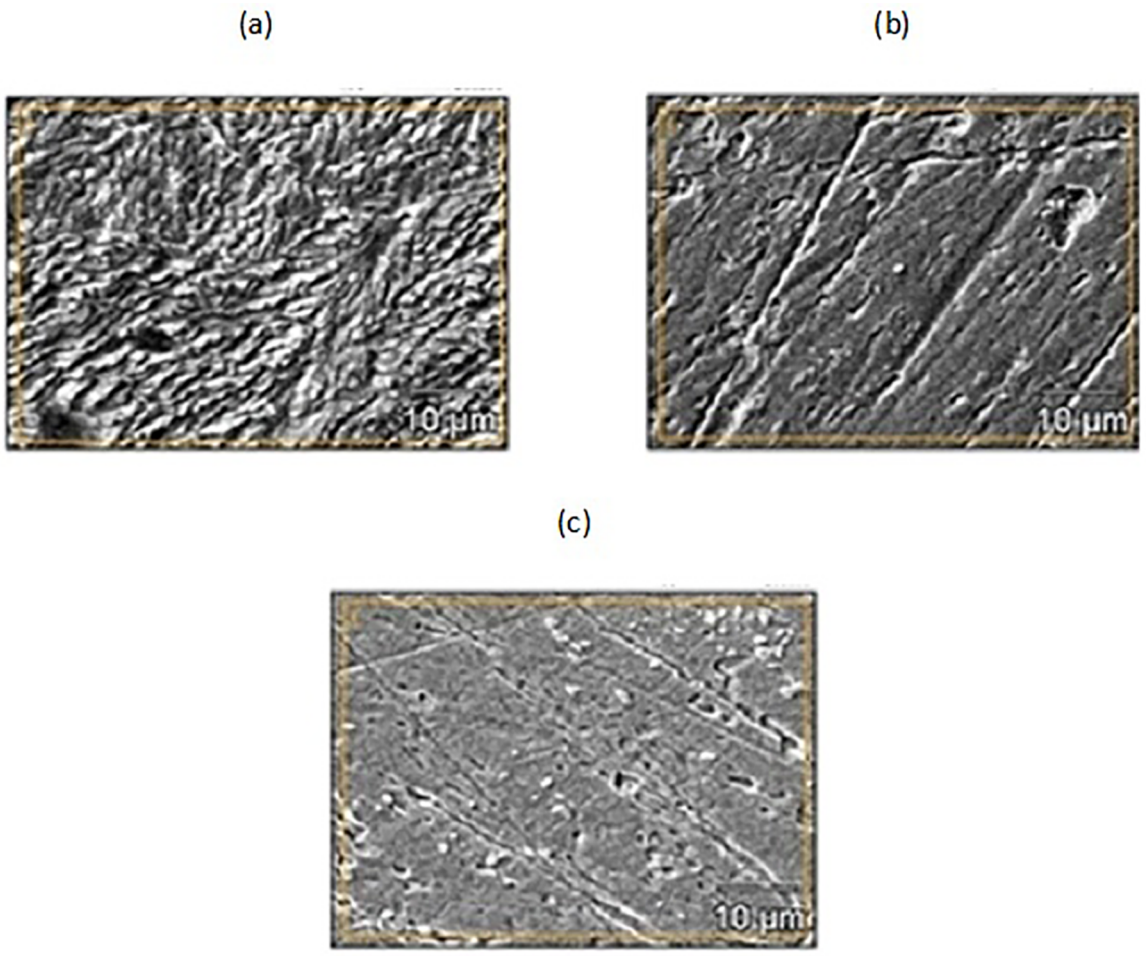


**Figure 7.** Morphological analysis of the mild steel surface in 1 mol $L^{-1}$HCl medium in the absence (A) and presence of the barley grain (B) and malting process residue(C) extracts. The image was magnified 2000 times.

**Table 7.** Weight loss measurements varying HMWF concentration for 2 h of immersion time.

| Immersion time (h) | HMWF (mg $L^{-1}$) | $W_{corr}$ (g $cm^{-2}h^{-1}$) | SD | *IE*(%) |
|---|---|---|---|---|
| | Blank | $2.74x10^{-3}$ | $5.6x10^{-5}$ | - |
| | 100 | $1.07x10^{-3}$ | $1.2x10^{-5}$ | 60.9 |
| **2** | 200 | $9.16x10^{-4}$ | $6.1x10^{-5}$ | 66.6 |
| | 300 | $7.99x10^{-4}$ | $5.4x10^{-5}$ | 70.8 |
| | 400 | $7.07x10^{-4}$ | $2.6x10^{-5}$ | 74.2 |

SD: standard deviation

was 74.2 for 400 mg $L^{-1}$ (Table 7). At the same conditions, the aqueous barley grain extract presented an inhibition efficiency of 82.2%.

Regarding the weight loss measurement in the absence and presence of HMWF, changing the temperature (Table 8 and Figure 8), the apparent activation energy associated with the corrosion process in the absence and presence of the HMWFextract was 38.7 and 31.5 kJ $mol^{-1}$, respectively (Table 9). The same behavior was observed for barley grain and malting process residue extracts, i.e., a decrease of $E_a$ and an increase of *IE* with the temperature, characterizing a chemical interaction between the molecules present in the HMWF and the steel surface. The activation parameters as $\Delta H^*$ and $\Delta S^*$ obtained in the absence and presence of HMWF were 36.1 and 28.9 kJ $mol^{-1}$ and -167 and -204 J $mol^{-1}$ $K^{-1}$, respectively (Table 9). As observed in the studied extracts, the value of the difference $E_a$-$\Delta H^*$ is 2.6 kJ $mol^{-1}$, which is equal to the average value of RT (2.6 kJ $mol^{-1}$) and indicates that the corrosion process is also a unimolecular reaction[40]. Again, the entropy of activation $\Delta S^*$ was negative both in the absence and presence of the inhibitor, implying that the activated complex represented the rate determining step with respect to the association rather than the dissociation step.

Figures 9a and 9b present the electrochemical impedance diagrams and the polarization curves performed in the absence and presence of 10, 100 and 200 mg $L^{-1}$ of HMWF. The same behavior was observed for the barley grain extract, i.e., an

**Table 8.** Weight loss measurements varying temperature in the absence and presence of 400 mg $L^{-1}$ of the HMWF after 4 h immersion time.

| | $W_{corr}$(Blank) (g $cm^{-2}h^{-1}$) | SD | $W_{corr}$ (HMWF)(g $cm^{-2}h^{-1}$) | SD | *IE*(%) |
|---|---|---|---|---|---|
| **25** | $5.12x10^{-3}$ | $3.9x10^{-5}$ | $1.10x10^{-3}$ | $4.4x10^{-5}$ | 78.5 |
| **35** | $1.00x10^{-2}$ | $6.1x10^{-5}$ | $1.90x10^{-3}$ | $2.5x10^{-5}$ | 81.0 |
| **45** | $1.43x10^{-2}$ | $5.0x10^{-4}$ | $2.60x10^{-3}$ | $6.3x10^{-5}$ | 81.8 |
| **55** | $2.21x10^{-2}$ | $3.5x10^{-4}$ | $3.60x10^{-3}$ | $1.8x10^{-4}$ | 83.7 |

SD: standard deviation

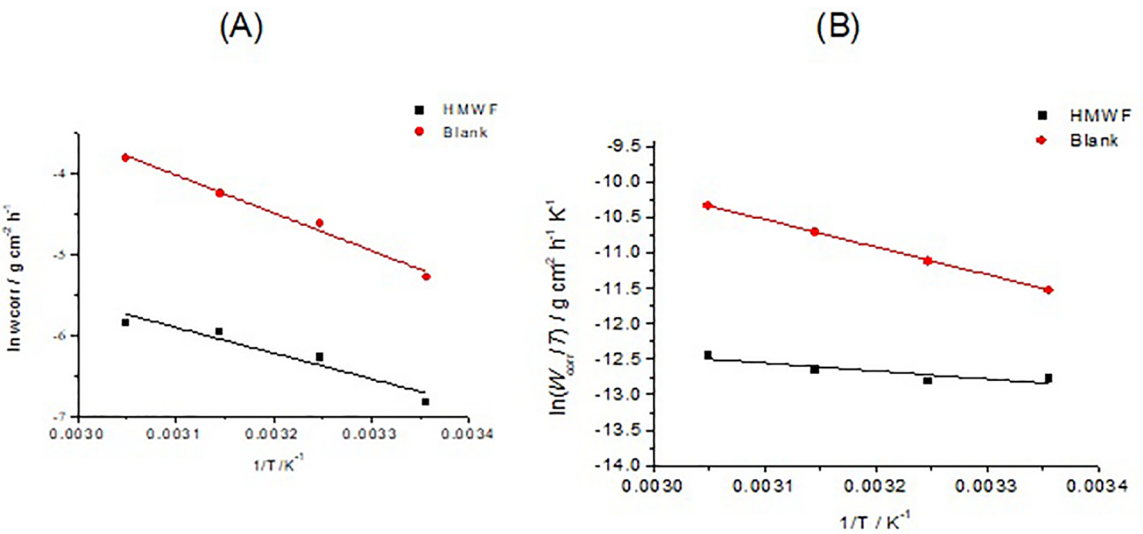


**Figure 8.** Arrhenius plots ln$W_{corr}$ x 1/$T$ (A) and ln ($W_{corr}$/$T$) x 1/$T$(B) for mild steel in 1 mol $L^{-1}$HCl in the absence and presence of the HMWF obtained from aqueous barley grain.

**Table 9.** Activation parameters ($E_a$, Δ$H$* and Δ$S$*) for mild steel corrosion in the absence and presence of 400 mg $L^{-1}$ of HWMF.

| ***Ea*(kJ $mol^{-1}$)** | | **Δ*H**(kJ $mol^{-1}$)** | | **Δ*S**(J K−1 $mol^{-1}$)** | |
|---|---|---|---|---|---|
| **Blank** | **Inhibitor** | **Blank** | **Inhibitor** | **Blank** | **Inhibitor** |
| 38.7 | 31.5 | 36.1 | 28.9 | -167 | -204 |

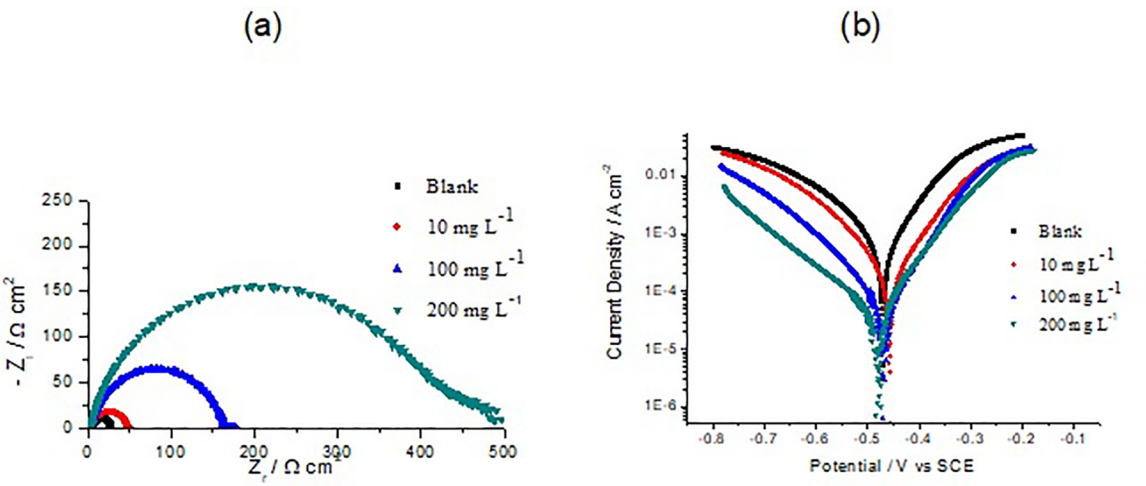


**Figure 9.** (A) Electrochemical impedance diagrams for mild steel in 1 mol $L^{-1}$ HCl media in the absence and presence of different extract concentrations of HMWF (B) Polarization curves for mild steel in 1 mol $L^{-1}$ HCl in the absence and presence of different extract concentrations of HMWF.

increase of the charge transfer resistance and a decrease of CPE1 with the HMWF concentration and the appearance of a second loop in the low-frequency range for higher inhibitor concentration (200 mg $L^{-1}$). The inhibition efficiencies were 45.2 and 94.5% for 10 and 200 mg $L^{-1}$ HMWF, respectively (Table 10). For 200 mg $L^{-1}$ barley grains extract the *IE* was 91.4% (Table 4).

Regarding the polarization curves, it was observed that the anodic and cathodic current densities were reduced in the presence of 10, 100 and 200 mg $L^{-1}$ HMWF, and the corrosion current density was lowered, resulting in *IE* reaching 63.8%, 90.6%,and 93.8%, respectively. The barley grains extract showed 91.3% of *IE* for 200 mg $L^{-1}$. As it was seen for barley grains extract, no significant changes in the values of the anodic and cathodic Tafel slopes were detected indicating that the HMWF does not change the anodic and cathodic mechanisms, responsible for the dissolution of the metal and the reduction of hydrogen, respectively (Table 11). This result seems surprising since the impedance diagrams results showed a second capacitive loop at the open circuit potential, which concludes that these extracts could change the corrosion mechanism.

Therefore, based on all the results with HMWF, we can conclude that the macromolecules such as proteins and/or polysaccharides, present in the HMWF, appear to be responsible for the inhibition action of the aqueous barley grain extract. The HMWF from gorse aqueous extract also presented high inhibition efficiency towards mild steel acid corrosion[45].

## 5. Conclusions

- Aqueous barley grains extract as well as their residue obtained from malting process act as an effective inhibitor to prevent corrosion of mild steel when present in a 1 mol $L^{-1}$HCl.
- The inhibition efficiency increased with the concentration of the extracts, immersion time and temperature.
- The action of the extracts as a corrosion inhibitor of the mild steel in acid solution can be attributed to the chemisorption by the molecules present in the extracts on the metal surface.
- Adsorption of the extracts followed a Langmuir adsorption isotherm.
- The electrochemical results obtained from measurements of electrochemical impedance suggest that adsorption of the inhibitors affects the corrosive mechanism involving an intermediary species with the inhibitory molecule.
- The total phenol content cannot be solely responsible for the corrosion inhibition of mild steel.
- Finally, based on the results of the high molecular weight fraction, it is possible to propose that macromolecules as proteins and/or polysaccharides are probably responsible for the inhibitory action observed by the aqueous extract of barley grains and the malting process residue.

**Table 10.** Electrochemical parameters obtained from the electrochemical impedance spectroscopy for mild steel in HCl in the absence and presence of HMWF from barley grains infuse.

| HMWF (mg $L^{-1}$) | $R_1$ ($\Omega$ $cm^2$) | n | $Y_1$ (mMho $cm^{-2}$) | $f_{max}$ (Hz) | $C_{dl}$ (µF $cm^{-2}$) | *IE*% |
|---|---|---|---|---|---|---|
| **Blank** | 23.6 | 0.998 | 102 | 71.6 | 101 | - |
| **10** | 43.1 | 0.998 | 72.1 | 56.7 | 71.3 | 45.2 |
| **100** | 160 | 0.997 | 42.0 | 26.3 | 41.5 | 85.3 |
| **200** | 426 | 0.996 | 26.0 | 13.9 | 25.6 | 94.5 |

**Table 11.** Electrochemical parameters obtained from the polarization curves for mild steel in HCl solution in the absence and presence of HMWF from barley grains infuse.

| Inhibitor (mg $L^{-1}$) | *OCP* (mV) | $E_{corr}$ (mV) | $\beta_a$ (mV $dec^{-1}$) | $-\beta_c$ (mV $dec^{-1}$) | $j_{corr}$ (mA $cm^{-2}$) | *IE*% |
|---|---|---|---|---|---|---|
| | | | **HMWF** | | | |
| **Blank** | -500 | -0.454 | 71.1 | 138 | 0.789 | - |
| **10** | -482 | -0.446 | 84.8 | 124 | 0.286 | 63.8 |
| **100** | -500 | -0.463 | 76.8 | 110 | 0.074 | 90.6 |
| **200** | -485 | -0.480 | 78.9 | 150 | 0.049 | 93.8 |

## 6. Acknowledgments

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