# The Possibility of Using Barley Grains Extract as an Acidic Corrosion Inhibitor for Carbon Steel

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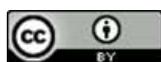
## Abstract

The effect of barley seed extracts on the corrosion of carbon steel in 1M hydrochloric acid at different temperatures was investigated from the perspective of their potential use as green inhibitors in the cleaning and descaling processes in heat exchangers. A 50% ethanol/water (vol) solution was used for extraction. Two extraction methods were used: soaking and ultrasound. The inhibition mechanism of the inhibitor that gave the best efficiency was investigated by studying the adsorption and corrosion processes by electrochemical methods (potentiodynamic polarisation (Tafel curves) and electrochemical resistance spectroscopy) and thermodynamic calculations. The results of the study showed no effect of the extraction method on the inhibition behavior, the inhibition as a function of concentration showed a significant increase in the inhibition efficiency up to concentration 400 ppm, then it appeared independent of it in both methods. However, the inhibition efficiency of the soaking method was higher at 800 ppm (87.01% compared to 80% for the ultrasound method). The study of the inhibition mechanism of this extract indicated the possibility of chemical adsorption. Inhibition activity increased with temperature.

**Keywords:** Acidic corrosion, Barley grains, Carbon steel, Corrosion inhibitors, Electrochemical tests, Extraction.

## Introduction

Metal corrosion, which leads to the gradual destruction of metal structures and equipment, is caused by the electrochemical and chemical reactions of the metal surface with the aggressive agents in the surrounding medium such as $H^+$, $Cl^-$, etc. to form more stable materials[1]. Corrosion causes various damages and large economic losses. As it causes the destruction of nearly a quarter of the annual production of steel, which is estimated at about 150 million tons annually, or 5 tons per second, economic losses represent 3–4 percent of the volume of gross national production in industrialized countries[2,3]. Corrosion is unavoidable[4], but it can be greatly reduced with proper prevention and protection measures. Procedures for inhibiting corrosion reactions by adding appropriate chemicals to the medium are gaining popularity in industrial applications[5], particularly in the protection of carbon steel, which is one of the most important alloys used in a wide range of industrial fields. In spite of the good mechanical characteristics of carbon steel and the low economic cost compared to other types of steel, and although some alloy additions may increase the steel's resistance to corrosion, it remains subject to severe corrosion in some media and conditions. Acidic media used in acid cleaning

processes, metal surface treatment during production, cleaning and descaling in heat exchangers, and revitalization of oil and gas wells are particularly severe corrosion media[6,7]. In such cases, the use of corrosion inhibitors is the most effective practical method for protecting metals from corrosion. Various organic and inorganic compounds, such as heterocyclic compounds composed of sulfur, oxygen, and nitrogen atoms have been discovered, synthesized, and used as corrosion inhibitors on metal surfaces. Although it was proven that these organic and inorganic synthetic inhibitors are effective in reducing corrosion rates, their use was limited due to the high cost of their production and the need for specific production techniques, in addition to their toxicity and danger to humans and the environment. Therefore, the possibility of finding effective corrosion inhibitors on the basis of available natural materials that are produced according to simple techniques and are environmentally friendly, also

known as "green alternatives" or "green inhibitors," is being researched widely at present to replace toxic or hazardous chemicals[8-11]. Plant extracts have received a lot of attention among the green inhibitors[12], and they are considered promising inhibitors because they are based on available materials, we can increase their production by developing their cultivation, and we can also increase their effectiveness by developing our knowledge of the active substances in them and their extraction processes[13].

Research Objective:
The scope of the study investigates the use of barley grain extract as green acid corrosion inhibitors (it is environmentally biodegradable and does not require complex manufacturing processes that generate waste that is harmful to the environment) for carbon steel in 1M HCl. determine the conditions of the extraction process and medium that provide the best corrosion protection for the metal.

## Materials and Methods

The study includes:
- Preparing barley grains extracts by means of normal soaking and ultrasound.
- Studying the effect of extracts prepared by the two methods on the corrosion of samples prepared from carbon steel in a (1M HCl) medium.
- Studying the inhibition mechanism of the extract that achieves the best corrosion inhibition efficacy in the field of study (through adsorption studies and electrochemical studies of corrosion).
- thermodynamic calculations for corrosion and inhibition processes at $25 - 45 - 70°C$ for 2 hours.

Equipment and Tools Used:
- Potentiostat "Gill AC 1395".
- Emission spectrum analyser "OES analyser SPECTROLAB S".
- Fourier transform infrared spectroscopy "4100-FT-IR".

- Ultrasonic water bath, frequency 40kHz, Chinese manufacture, model "PS-80A".

Materials Used in the Research:
- Target plant: barley grains.
- The Chemicals are shown in Table 1.

**Table 1. Chemicals**

| Raw materials | Supplier | Purity |
|---|---|---|
| hydrochloric acid | Sigma-Aldrich | 36% Analytical Grade |
| ethanol | Scharlau | Analytical Grade |
| lead acetate | Ladd | Analytical Grade |
| ferric chloride | Sigma-Aldrich | Analytical Grade |
| potassium hydroxide | Sigma-Aldrich | Analytical Grade |

Preparation of Mineral Samples:
The laboratory study was carried out on steel samples matching the shell of the E1 heat exchanger from Unit 21 of the Homs Refinery. Emission spectra analysis of the mineral samples showed the chemical composition as shown in Table 2.

**Table 2. Chemical composition of carbon steel samples.**

| C % | Si % | Mn % | P % | S % | Cr % | Mo % |
|---|---|---|---|---|---|---|
| 0.42 | 0.2051 | 0.764 | 0.0371 | 0.0232 | 0.0318 | <0.0020 |
| Ni % | Al % | Co % | Cu % | Nb % | Ti % | V % |
| 0.0415 | <0.0005 | 0.0133 | 0.0588 | <0.0021 | <0.0005 | 0.0055 |
| W % | Sn % | As % | Zr % | Ca % | Ce % | Sb % |
| <0.0050 | 0.0036 | 0.0313 | <0.0010 | <0.0010 | <0.0030 | 0.011 |
| Ta % | B % | N % | Fe % | | | |
| <0.0050 | <0.0002 | <0.0010 | 98.34 | | | |

The carbon steel samples were cut mechanically with dimensions:
-3.8 * 2.7 * 0.5 cm for gravimetric tests.
-3 * 0.7 * 0.5 cm for electrochemical tests.

After which the surface was cleaned and polished using sandpaper with graduated sizes 80-100- 180- 600- 800 mesh respectively, until the surface became smooth. The samples were then washed with water, cleaned with a rubber pad, and then washed with acetone to remove any fatty substances that may have been present on their surfaces. The samples were dried in an electric desiccator; after which they were exposed to the corrosive medium.

Preparation of Plant Extracts:
Reference studies show that barley grains contain high levels of polyphenols. Based on data confirming the role of phenol groups with corrosion inhibition properties, barley grains were chosen as the study material. The extractions were carried out on barley grains in an aqueous solution of 50% ethanol (vol/vol), which is characterized by the extraction of low molecular weight polyphenols and polar phenolic compounds, which are active compounds with a significant inhibitory effect.

Initially, the grains were ground using a mill. The percentage distribution of the dimensions of the grains of the crushed grains used in extraction is shown in Table 3.

**Table 3. Sieving classification of barley grain after milling.**

| Sieving classification | Barley Grain % |
|---|---|
| ≥1.6 mm | 1.8 |
| 1.6mm-710 Mic* | 21.0 |
| 710-300 Mic | 65.0 |
| 300-150 Mic | 11.0 |
| ≤150 Mic | 1.2 |

\* Mic: Micro meter

A grains extract was prepared with a solid: liquid ratio (1 gram of plant:10 gram of 50% ethanol) of by two methods, soaking and ultrasound, at 50°C for 2

hours, then left at a laboratory temperature of $25°C$ for 24hours. The extract was filtered and then dried using an air dryer at $25°C$, for three days. Table 4 shows the extraction percentage in each of the two methods.

**Table 4. Weight percentage of barley grains extract.**

| Extract symbol | Method | % extraction percentage |
|---|---|---|
| G1 | Ultrasound | 12.3 |
| G2 | Soaking | 9.34 |

Corrosion Tests:
Gravimetric and electrochemical tests were carried out to determine the corrosion rate. Despite the existence of modern electrochemical techniques that allow accelerated corrosion tests, gravimetric tests give a clearer idea of the changes occurring in the system (metal/medium) with time, especially since corrosion itself is a time-dependent process.[14-15]

Weight Loss Measurements Tests:
The corrosion of the mineral samples was studied after their preparation, drying, and weighing before immersing them in (1M HCl) medium at a laboratory temperature of 25°C, for 24 hours in 200 ml of an acidic solution. The samples were washed with distilled water, dried, and the post-immersion weight was recorded after the test period ended. The corrosion rate (CR) is calculated according to Eq.1[16]:

$$CR = \frac{w_1 - w_2}{At} \qquad 1$$

where CR: corrosion rate (g/cm$^2$h$^1$), w1: weight of the mineral sample before exposure to the corrosive medium (g), w2: weight of the mineral sample after exposure to the corrosive medium (g), A: surface

area of the mineral sample (cm$^2$), and t: immersion time (h).

The degree of protection (inhibitor effectiveness) provided by the Ƞ% inhibitor is given by Eq.2[16]:

$$\text{Ƞ}\% = \frac{CR_0 - CR_1}{CR_0} \times 100\% \qquad 2$$

Where $CR_0$ ، $CR_1$ is the corrosion rate (g/cm$^2$h) in the absence and presence of the inhibitor, respectively.

Potential Dynamic Polarization (PDP):
PDP is electrochemical method for measuring corrosion rate, inhibitor efficiency, and understanding corrosion protection mechanisms is potential dynamic polarization measurements [17].

Electrochemical experiments for potential dynamic polarization were carried out using a three-electrode model cell under natural ventilation conditions. After immersing the working electrode in the test solution for 66 minutes until the open circuit potential (OCP) was reached(*we get to OCP when* $(\Delta E_{corr}/t) = 5mV/min$), the polarization curves were recorded at a constant scan rate of 0.66 mV/s for the field $\pm 325$ mV around the corrosion potential of the metal sample E$_{corr}$.

Eq.3 gives effectiveness of the inhibitor[17]:

$$\text{Ƞ}\% = \frac{\text{i}^0_{\text{Corr}} - \text{i}^1_{\text{Corr}}}{\text{i}^0_{\text{Corr}}} \times 100\% \qquad 3$$

where $\text{i}^0_{\text{corr}}$, $\text{i}^1_{\text{corr}}$ are the corrosion current density values in the absence and presence of the inhibitor.

Electrochemical Impedance Spectroscopy (EIS):

EIS is a useful technique for monitoring in-situ electrochemical changes because it provides information on physical processes that occur at the metal-electrolyte interface, such as electrode kinetics, surface properties, and mechanism[17].

Electrochemical impedance measurements were performed using an alternating current signal with a wave amplitude of 32 mV (peak-to-peak) at an open-circuit potential in a frequency range from 4.5 kHz to 10 mHz. Under natural ventilation conditions at a laboratory temperature of $25°C$ In a typical three-electrode cell.

Eq. 4 calculates the degree of protection (Ƞ %) based on the EIS data[18]:

$$\text{Ƞ}\% = 1 - \frac{R^o_{ct}}{R^1_{ct}} \times 100 \qquad 4$$

where $R^1_{ct}$ و $R^o_{ct}$ are the charge transfer resistance in the presence and absence of the inhibitor, respectively.

## Results and Discussion

Results of Weight Loss Tests
Gravimetric tests were carried out on mineral samples to measure corrosion speed without an inhibitor, and when there were different concentrations of the inhibitor (0, 200, 400, 600, 800 and 900 ppm) for the prepared extracts G1 and G2, the degree of protection was calculated.
The results of the gravimetric tests for extracts G1 and G2 are presented in Table 5, these results are presented graphically in Fig 1.

**Table 5. Gravimetric test results for extracts G1 and G2**

| inhibitor concentration (ppm) | Corrosion rate (g/cm$^2$h$^1$) | Degree of protection Ƞ % |
|---|---|---|
| **G1 extract in 1M hydrochloric acid medium** | | |
| 0 | 0. 330 | --- |
| 200 | 0. 172 | **47. 90** |
| 400 | 0. 059 | **82. 02** |
| 600 | 0. 063 | **80. 85** |
| 800 | 0. 064 | **80. 53** |
| 900 | 0.052 | **84.0** |
| **G2 extract in 1M hydrochloric acid medium** | | |
| 0 | 0. 330 | --- |
| 200 | 0. 189 | **42. 83** |
| 400 | 0. 052 | **84. 22** |
| 600 | 0. 049 | **85. 13** |
| 800 | 0. 043 | **87. 01** |
| 900 | 0.124 | **62.17** |

According to Table 5 both extracts have an inhibitory effect on acid corrosion of carbon steels in (1M HCl).

The G1 and G2 extraction method did not affect the general behavior of the activity of the plant extract with the concentration, so in both cases we see a significant increase in the inhibition efficiency with the concentration up to 400 ppm, then it appears independently.
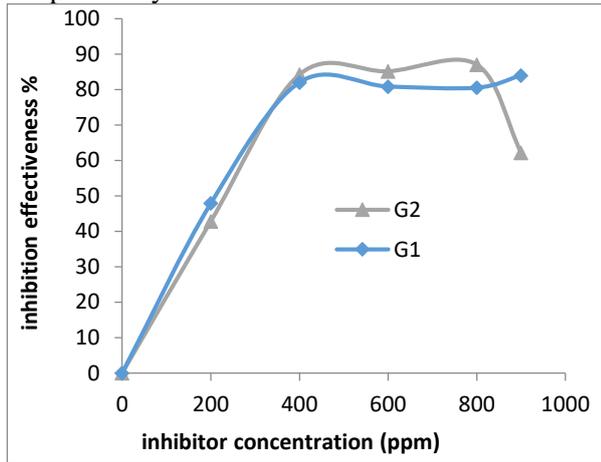


**Figure 1. Inhibition activity of Barley grains extract G1, G2 in (1M HCl) with immersion period of 24 hours at 25℃.**

The value of the degree of corrosion protection provided by the plant extract was affected by the extraction method, so the soaking extract G2 was characterized by a better degree of protection, especially at the optimum concentration of 800 ppm (87.01% compared to 80.56% for extract G1). This may be due to the possibility of degradation of some active compounds under the influence of ultrasonic waves.

Maceration process gave an inhibitor with a better degree of protection, so the study of the mechanism of inhibition was limited to this inhibitor.

Adsorption Study

Adsorption of active compounds is often the first step in inhibition. Thus, the inhibitory action of plant extracts is often explained based on molecular adsorption. Isothermal adsorption is used to describe the interactions of inhibitor molecules with active sites on a metal surface. There are many mathematical models that express isothermal adsorption and that estimate the amount of adsorption (i.e. inhibitor molecules or ions) on the adsorbent (i.e. metal surface) at a constant temperature, such as Langmuir, Temkin, Frumkin, Freundlich, Flory–Huggins,and Bockris–Swinkels. Table 6 presents the mathematical equations for this isothermal adsorption[19].

**Table 6. Mathematical representation of isothermal adsorption**

| Isotherm | mathematical models | Liner form |
|---|---|---|
| Langmuir | $log\left(\frac{C}{\theta}\right) = \log C - \log K_{ads}$ | $log\left(\frac{c}{\theta}\right)$ VS $\log C$ |
| Freundlich | $log\left(\frac{C}{\theta}\right) = \log K_{ads} + \text{n} \log(1-\theta)$ | $log\left(\frac{c}{\theta}\right)$ VS $\log(1-\theta)$ |
| Frumkin | $log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + \text{y} \log (C)$ | $log\left(\frac{\theta}{1-\theta}\right)$ VS $\log C$ |
| Temkin | $\theta = B \log K_{ads} + B log\, C$ | $\theta$ VS $log\, C$ |
| Harken-Jura | $\frac{1}{\theta^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log\, C$ | $\frac{1}{\theta^2}$ VS $\log\, C$ |
| Dubinin-Radushkevich | $log(\theta) = \log K_{ads} + K_{DR}\,(\varepsilon)^2$ | $log(\theta)$ VS $(\varepsilon)^2$ |
| Elovich | $log\left(\frac{\theta_e}{C}\right) = \log K_e q_m - \frac{\theta_e}{\theta_m}$ | $log\left(\frac{\theta_e}{c}\right)$ VS $\frac{\theta_e}{\theta_m}$ |

Applying the previous mathematical equations expressing isothermal adsorption to the values obtained from gravimetric experiments for extract G1 and G2, we find that G1 is subject to Langmuir adsorption and G2 is subject to Frumkin adsorption in the range 0-400 ppm with a correlation coefficient of $R^2 = 0.96$ and Langmuir adsorption in the range 400-900 ppm with a correlation coefficient of $R^2 = 0.91$, as shown in Fig 2 and Fig 3.

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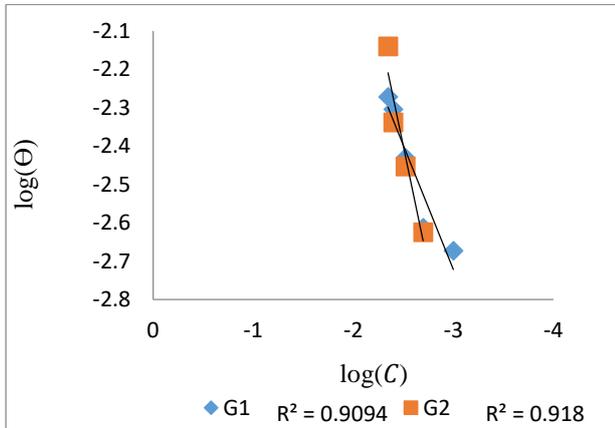


**Figure 2. Langmuir adsorption of G1 and G2 extract in (1M HCl) at 25^OC.**
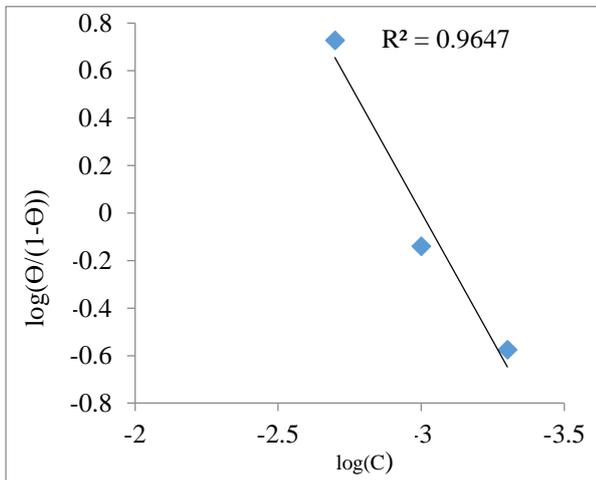


**Figure 3. frumkin adsorption of G2 extract in (1M HCl) clover the range (0-400) ppm at 25^OC.**

The inhibition process can be largely explained by isothermal adsorption. The study was completed by using supporting electrochemical techniques to study the effect of the inhibition process on the electrochemical properties of the system.

Potentiodynamic Polarization PDP
The dynamic polarization curve of carbon steel in 1M hydrochloric acid in the absence and presence of different concentrations of G2 at $25°C$ is shown in Fig 3.

The electrochemical indices (corrosion potential $E_{corr}$, corrosion current density $i_{corr}$, and slope for Tafel curves of cathodic and anodic polarization ($\beta c$, $\beta a$)) that were calculated using the analysis software attached to the tester are shown in Table 7.
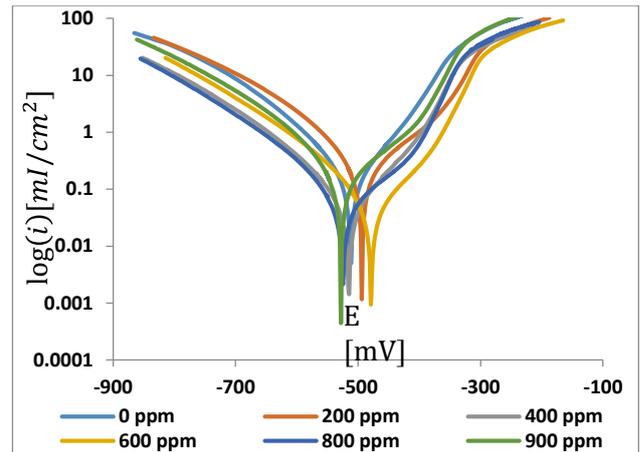


**Figure 3. Tafel diagram of carbon steel samples in a medium of (1M HCl) the absence and presence of different concentrations of G2 inhibitor at 25°C.**

Table 7 shows that the change in corrosion potential in the presence of the inhibitor was less than 85 mV than absence of the inhibitor (0 ppm) at all concentration (200-400-600-800-900) ppm, indicating that the extract G2 is a mixed-type inhibitor[20,21]. Furthermore, no discernible change in the values of the anodic and cathodic Tafel constants was observed, indicating that the mechanism of iron dissolution and hydrogen evolution is not altered by the participation of the inhibitors[22,23], but rather by blocking the surface and changing the composition of the electric double layer, thereby impeding charge transport.

**Table 7 Electrochemical indices of carbon steel in (1M HCl) in absence and presence of different concentrations of G2 extracts at $25°C$ obtained from potentiodynamic polarisation (Tafel curves).**

| Concentraction inhibitor | $E_{corr}$[mV] | $i_{corr}$ [mA/cm$^2$] | $\beta_a$ [mv/dec] | $-\beta_C$ [mv/dec] | η % |
|---|---|---|---|---|---|
| 0 ppm | -540. 6 | 0. 36 | 94. 4 | 163. 6 | 0 |
| 200 ppm | -508. 8 | 0. 22 | 88. 9 | 144. 3 | 38. 8 |
| 400 ppm | -526. 8 | 0. 058 | 80. 9 | 130. 9 | 83. 8 |
| 600 ppm | -487. 8 | 0. 054 | 76. 8 | 131. 6 | 85. 0 |
| 800 ppm | -530. 4 | 0. 049 | 74. 2 | 133. 9 | 86. 3 |
| 900 ppm | -535. 8 | 0. 13 | 81. 1 | 131. 1 | 63. 8 |

## Electrochemical Impedance Spectroscopy

Figure 3 depicts Nyquist curves for carbon steels in a 1 M hydrochloric acid solution in the absence and presence of various concentrations of extractive G2 at $25°C$.

The Nyquist electrochemical impedance graphs in most cases do not show a perfect semicircle due to frequency dispersion, as a result of surface roughness or inhomogeneity due to inhibitor adsorption.
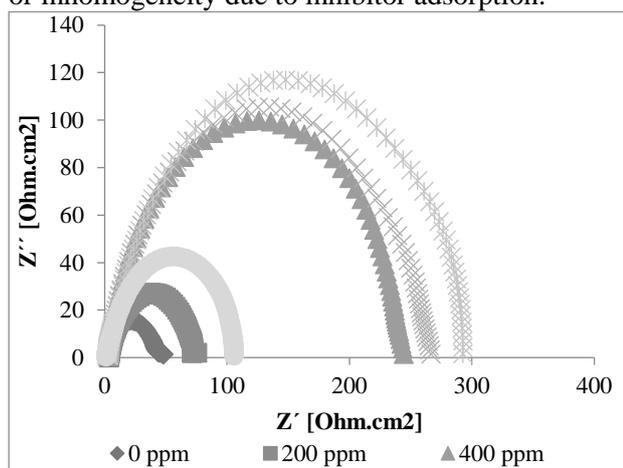


**Figure 3. Nyquist curves of carbon steel samples**

**absence and presence of different concentrations of G2 extracts in (1M HCl) at 25°C.**

While these curves show a single capacitive loop, indicating that the steel corrosion process is primarily controlled by the charge transfer process[23], its diameter increases as the inhibitor concentration increases due to an increase in the charge transfer resistance.

The Nyquist diagram was analyzed by concordance of the experimental data with a simple equivalent circuit model, which includes the solution resistance Rs and the double layer capacitance Cdl placed in parallel with the charge transfer resistance Rct through analysis software as well. The calculated Nyquist chart data are shown in Table 8.

**Table 8. Electrochemical impedance spectroscopy indices and inhibition efficacy of carbon steel samples in absence and presence of different concentrations of G2 extracts in (1M HCl) at 25°C.**

| Concentration inhibitor | $R_{ct}$ [Ω.cm²] | $R_{sol}$ [Ω.cm²] | $C_{dl}$ [ μF ] | ɳ % |
|---|---|---|---|---|
| 0 ppm | 39 | 2. 66 | 175 | 0. 00 |
| 200 ppm | 68. 6 | 3. 13 | 289 | 0. 43 |
| 400 ppm | 246 | 2. 61 | 148 | 0. 84 |
| 600 ppm | 262 | 3. 25 | 150 | 0. 85 |
| 800 ppm | 298 | 2. 98 | 185 | 0. 87 |
| 900 ppm | 106 | 1. 06 | 425 | 0. 63 |

From Table 8, it is noted that the charge transfer resistance increased with the increase of the inhibitor concentration, and this is consistent with the study of adsorption and Tafel curves through surface coverage.

We do not find a specific behavior of the capacitance of the double layer, and this may be due to the nature of the effect of the inhibitor on the double layer and the local dielectric constant, that is, on the arrangement of charges inside the electrical double layer and on the metal surface.

## FT-IR Analysis

The FT-IR analysis technique was used to evaluate the composition of the G2 plant extract and to verify

the bonds and functional groups present in the extract, supported by the qualitative detection of phenols, flavonoids, and saponins.

Fig 4, depicts the analysis of the FT-IR spectra of barley grains extract using the ethanol soaking method G2. The results of the qualitative analysis are also shown in Table 9.

The broad and very strong absorption band at wave number 3400 cm⁻¹ is attributed to the N–H or O–H expansion of the phenolic group. The absorption band at 2929 cm⁻¹ is attributed to the stretching of the unsaturated C–H bond. Whereas the absorption band at 2361 cm⁻¹ is related to the S-H bond expansion in thiols. Concerning the stretching vibration absorption band at 1740 cm⁻¹ associated with the

C=O bond. The absorption band at 1617 cm⁻¹ is attributed to the expansion of the C=C aromatic ring. The banding at 1416 cm⁻¹ can be attributed to the angle distortions of the C-H or S=O. The band at 1272 cm⁻¹ is attributed to the C-O or N-H stretching of the amino acids. The absorption band at 1044-1121 cm⁻¹ can be assigned to C-O of primary alcohol deformations.
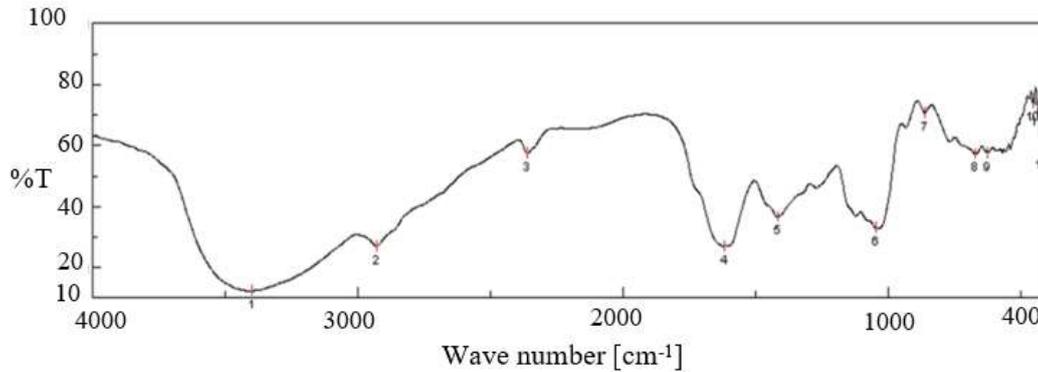


**Figure 4. FT-IR spectra of an ethanol-soaked barley grains extract G2**

The FT-IR analysis of the bonds and functional groups that are active and effective in inhibiting acid corrosion of carbon steels, especially the S-H bond, agrees with references[24,25].

The results of the qualitative detection analyses also agree with many studies conducted on plant extracts as inhibitors of acid corrosion of carbon steel in the presence of phenols, flavonoids, and tannins[25].

**Table 9. The qualitative analysis**

| revealing of | Detector type | G2 |
|---|---|---|
| Phenols | iron chloride | + |
| Tannins | lead acetate | + |
| Flavonoids | Alcoholic solution 10% potassium hydroxide | + |
| Terpenes | Shake the extract after adding distilled water | + |

**Studying the Thermodynamic and Kinetic Variables of the Corrosion Process:**
The thermodynamic study of the corrosion process was carried out at three different temperatures, where the corrosion speed was determined at temperatures $45^0C, 25^0C$ $70^0C$ by weight loss method by immersing 2 hours of the inhibitor G2 in a medium of 1M hydrochloric acid under reflux condenser.

**Table 10. Corrosion speed and inhibition effectiveness in the absence and presence of 800ppm of G2 at 25, 45,70oC by weight loss method for 2h.**

| Temperature | 25ºC | 45ºC | 70ºC |
|---|---|---|---|
| Corrosion speed in the absence of an inhibitor | 0.185 | 0.664 | **8.847** |
| Corrosion speed in the presence of the inhibitor concentration of 800ppm | 0.158 | 0.401 | **3.859** |
| inhibition efficacy | 14.8 | 39.6 | **56.4** |

Table 10 and Fig 5 present the effect of temperature on the corrosion rate of the studied carbon steels in the absence and presence of G2 inhibitor in 1M HCl.

The activation energy value is calculated based on the corrosion rate by the Arrhenius Equation in Eq 5:

$$CR = A\exp\left[\frac{-E_a}{RT}\right] \qquad 5$$

Where CR: corrosion rate, R: general gas constant (8.314 Jmol-1K-1), T: absolute temperature and A: exponential-Pre factor. Using the logarithm of both sides of the Arrhenius equation, we find Eq 6:

$$\ln(CR) = \ln(A) - \frac{-E_a}{RT} \qquad 6$$

Plotting the values of ln(CR) vs T/1 we get a straight line, the slope of which is -Eₐ/R and the point of intersection is ln(A). From the equation of state Eq 7,

the adsorption enthalpy is obtained. $\Delta H_{ads}$ and adsorption entropy $\Delta S_{ads}$.

$$CR = \frac{RT}{Nh} exp \left[\frac{\Delta S_a}{R}\right] exp \left[\frac{-\Delta H_a}{RT}\right] \qquad 7$$

Where N represents Avogadro's number ($6.02 \times 10^{23}$ mol) and h is Planck's constant ($6.63 \times 10^{-34}$ JS). By taking the logarithm of both sides of the equation of state, we get Eq. 8:

$$\ln\left(\frac{CR}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left[\frac{\Delta S_a}{2.303R}\right] - \left[\frac{\Delta H_a}{2.303RT}\right] \qquad 8$$

Graphing the values of $\ln$(CR/T) vs. 1/T, we get a straight line with a slope $-(\Delta H_a/(2.303RT))$ and the point of intersection is $\ln$(R/Nh)+($\Delta S_a$/(2.303R)) The following equation is used to calculate the free energy of adsorption.

The graphic representation of the Arrhenius equation for the corrosion process in the presence and absence of inhibitor G2 is shown in Fig 6.

Fig 7 depicts a graphic representation of the equation of state for the corrosion process in the presence
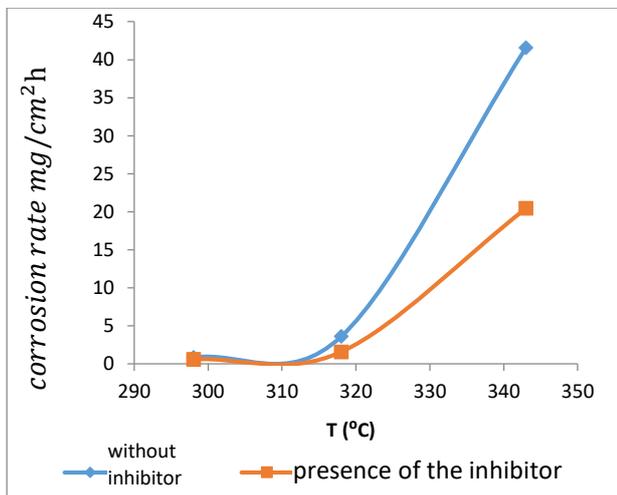
**Figure 5. Effect of temperature on corrosion rate in the absence and presence of 800ppm of G2 (1M HCl)**
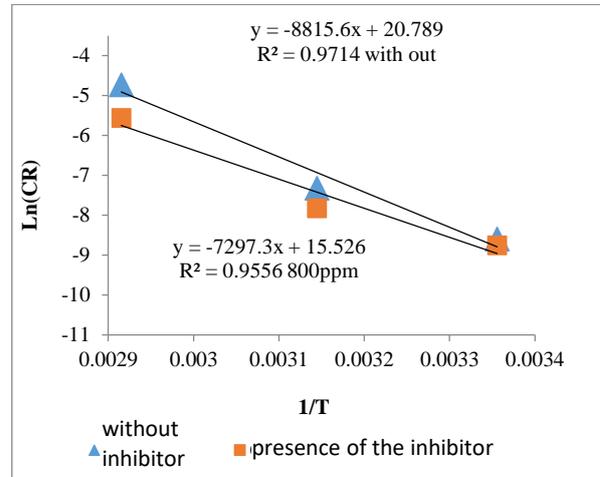
**Figure 6. Graphing of the Arrhenius equation**
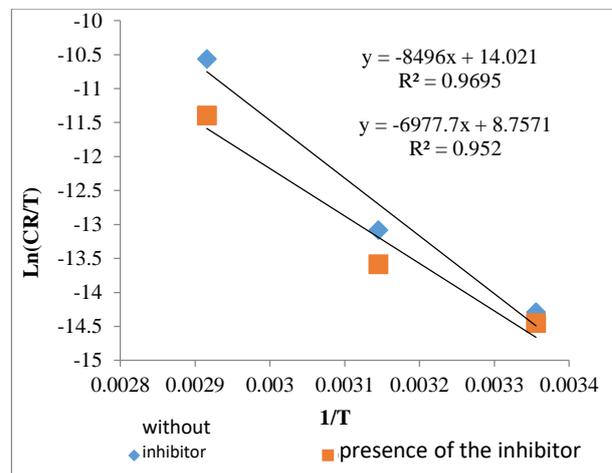
**Figure 7. Graph of the equation of state**

Table 11 presents the activation indices of G2 extract in a 1M medium of hydrochloric acid in the presence and absence of 800 ppm.

**Table 11. Parameters of activation of corrosion processes in 1M medium of hydrochloric acid in the presence and absence of 800ppm of G2 extract**

| Concentration ppm | activation energy kJ/mol | Enthalpy kJ/mol | Entropy kJ/mol.K |
|---|---|---|---|
| 0 | +73. 292 | +70. 640 | -0. 313 |
| 800 | 60. 667+ | 58. 012+ | -0. 270 |

It should be noted that the degree of protection increased with time, from 14.8% when immersed for 2 hours to 87.01% when immersed for 24 hours. This can be explained by the possibility of the inhibitor adsorbed on the surface of the metal interacting according to an electrochemical reaction, leading to the formation of new products with a higher inhibitory effect[26].

From Table 11, it is noted that the rate of acid corrosion of carbon steel increased in the studied medium with an increase in temperature. Table 11 shows that the enthalpy change of the dissolution process is positive, $\Delta H = +70.640$ kJ/mol, indicating that it is an endothermic process, and that the speed of the process increases with increase temperature.

It is noted from Table 11 that the value of activation energy in the presence of the inhibitor is less than its absence with an increase in the effectiveness of inhibition, as the activation energy decreased in the presence of inhibitor G2 at a concentration of 800 ppm from $Ea = +73.292$ kJ/mol to $Ea = +60.667$ kJ/mol. This decrease in the activation energy may indicate the presence of chemical adsorption of the extract on the surface of the carbon steel[27].

This can also be explained by the fact that at the upper limit of temperatures, the surface covered with the inhibitor increases, and the step controlling the dissolution of the metal becomes diffusion through the film of the corrosion products and the inhibitor. Thus, the dissolution rate is the sum of the two corrosion rates: the corrosion rate of the exposed metal surface and the corrosion rate of the surface

covered with the adsorbent inhibitor. In the case of high surface coverage, the first process does not have much contribution. In this case, the corrosion mechanism involves a direct interaction of the inhibitor molecules with the metal surface, and the activation energy can be smaller or higher than in the absence of the inhibitor. It should be noted that this activation energy includes the energy expended on charge rearrangement, as a result of adsorption, in the double layer.

We also find that values of Ea are larger than similar values of $\Delta H$, indicating that the corrosion process must involve a gaseous reaction, simply a hydrogen evolution reaction, which is associated with a decrease in the total reaction volume.

Whereas, the change in the entropy of the system in the presence and absence of the inhibitor was negative, which indicates that the system tends more to be organized in the sense that the intermediate component of the reaction results from a union stage to form the complex, not a dissociation stage. This means that the decrease in entropy continues to shift from the reactants to the intermediate compound.

## Conclusion

50% ethanol extract from barley grains can inhibit the acid corrosion of carbon steel in 1M hydrochloric acid.

The general inhibition efficiency behaviour of the barley grain extract is similar when extracted by the soaking and ultrasonic methods. The barley grain ultrasound extract provides better corrosion protection. The protective efficacy reaches 87.01% at 800 ppm for the soaking extract, compared to 80.0% for the ultrasonic extract at the same concentration. The studied soaking extracts act as mixed-type adsorption inhibitors. The adsorption of the barley grains ultrasound extract with ethanol is

subject to the Langmuir adsorption function with a correlation coefficient of $R^2 = 0.91$ over the range 0-900 ppm; the barley grains soaking extract with ethanol is subject to the Frumkin adsorption function with a correlation coefficient of $R^2 = 0.96$ over the range 0-400 ppm; and the Langmuir adsorption function with a correlation coefficient of $R^2 = 0.91$ over the range 400-900 ppm. Thus, the action of the extract as a corrosion inhibitor for carbon steel in an acidic solution can be attributed to chemisorption. The corrosion inhibition efficacy of barley grains soaking extract with ethanol solvent increased with increasing temperature within the study field.

## Acknowledgment

## Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been

included with the necessary permission for re-publication, which is attached to the manuscript.
- The author has signed an animal welfare statement.
- Authors sign on ethical consideration's approval.

- Ethical Clearance: The project was approved by the local ethical committee in Al-Baath University, Syria.

## Authors' Contribution Statement

B. A. contributed to the design and implementation of the research. B A. and F R. wrote the manuscript and discussed the results. Y J. commented on the manuscript.

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# إمكانية استخدام مستخلص بذور الشعير كمثبط للتآكل الحمضي للفولاذ الكربوني

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## الخلاصة

تمت دراسة تأثير مستخلصات بذور الشعير على تآكل الفولاذ الكربوني في $1M$ حمض كلور الماء للتحقق من إمكانية استخدام كمثبط أخضر في عملية التنظيف وإزالة الترسبات الحمضية للمبادلات الحرارية، عند درجات حرارة مختلفة. أجريت عمليات الاستخلاص باستخدام الايثانول والماء 50% حجماً، وبطريقتي النقع والأمواج فوق الصوتية. تمت دراسة آلية تأثير المثبط الذي أعطى كفاءة أفضل تثبيط، من خلال دراسة الامتزاز والتآكل بالطرق الكهروكيميائية (مخططات تافل، ومطيافية المقاومة الكهروكيميائية) والحسابات الترموديناميكية. أظهرت نتائج الدراسة عدم وجود تأثير لطريقة الاستخراج على سلوك التثبيط ، حيث أظهر التثبيط كدالة للتركيز زيادة معنوية في كفاءة التثبيط حتى التركيز 400 جزء في المليون ، ثم ظهرت مستقلة عنها في كلتا الطريقتين ، ومع ذلك كانت درجة الحماية أعلى لمستخلص طريقة النقع عند التركيز 800ppm (87.01% مقارنة بـ 80.56% لمستخلص الأمواج فوق الصوتية). أشارت دراسة آلية التثبيط لهذا المستخلص إلى إمكانية الامتزاز الكيميائي للمستخلص وإعادة لترتيب الشحنات في الطبقة المزدوجة الكهربائية . أبدت فعالية التثبيط ارتفاعاً مع درجة الحرارة.

**الكلمات المفتاحية:** التآكل الحمضي، بذور الشعير، الفولاذ الكربوني، مثبطات التآكل، الاختبارات الكهروكيميائية، الاستخلاص.