Corrosion Resistance of Mild Steel in Hydrochloric Acid Solutions by *Clinopodium acinos* as a Green Inhibitor

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Abstract: Study of corrosion inhibition for mild steel in 1M HCl by *Clinopodium acinos* (CA) extract was evaluated by altered methods. These methods are WL, electrochemical tests (Electrochemical frequency modulation (EFM), potentiodynamic polarization (PP), and electrochemical impedance spectroscopy (EIS)) and surface examination performances (AFM, ATR-FTIR and XPS). The CA extract concentrations are (50, 100, 150, 200, 250, 300 ppm) at altered temperatures 25, 30, 35, 40, 45 °C. WL curves showed raising the inhibition efficiency of M-S by increasing CA concentration and lowering the temperature. PP curves explained that CA extract act as a mixed type inhibitor. The green inhibitor was utilized because of its lower price and not affect the environment.

Keywords: M-S; CA; Corrosion inhibition; HCl; WL; PP; EIS; EFM; AFM; ATR-FTIR; XPS.

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1. Introduction

Metal corrosion occurs as a result of oxidation-reduction reactions found in the environment surrounding the metal [1]. MS is one of the metals used in industrial applications. It is used for handling of alkaline, acids, and salt solutions [2]. Acidic solutions are the most commonly used in the industrial process as like pickling, cleaning, descaling [3]. Various types of inhibitors are utilized to protect the corrosion of MS in acidic solutions. Nowadays a plant extracts (a green inhibitor) are the most utilized due to it is not expensive and not damage the environment [4]. The molecules of the inhibitor were adsorbed on the metal surface and block the active site due to prevent anodic and cathodic reactions [5].

In this study, CA extracts were utilized to inhibit the corrosion of MS in 1M HCl. Many altered tests are utilized to study the protection efficiency of CA. In WL and electrochemical tests, the corrosion rate rises with the increase of the CA extract concentration. The surface of the metal is premeditated by AFM, ATR-FTIR, XPS.

2. Materials and Methods

2.1. Composition of M-S sample.

The chemical elements present in the S sample recorded in Table (1):

| wt%  | C   | Si  | Mn     | S     | Cu  | P    | Ni     | Fe |
|------|-----|-----|--------|-------|-----|------|--------|----|
| M-S  | 0.17| 0.24| 0.7-0.9| 0.04  | 0.036| 0.006| 0.025 | the rest |
2.2. Chemicals.

2.2.1. Inhibitor.

The leaves of “CA were collected and dried at room temperature then ground to a fine powder using an electrical mill. (200g) of this powder soaked in 800 ml methanol, and then the methanolic extract of the sample was concentrated to near dryness under vacuum by using the rotary evaporator at 45 °C and got a stock of methanolic extract. The investigated extract was liquefied in ethanol (1g/L) and conserve into the refrigerator. We use the solution (1000 ppm) to prepare different concentrations of CA extract (50, 100, 150, 200, 250, 300 ppm)” [6].

Known commonly as basil thyme and spring savory, is a species of plant of the genus Acinos. It is a perennial that usually grows about 8 inches (20 cm) high and spreads 12 inches (30 cm). It prefers to grow in strong sunlight. Acinos arvensis is recorded as a food plant for the larva of the moth Coleophora tricolor. This plant is classified by Rose (The Wildflower Key, revised 2006) as Clinopodium acinos (Scheme 1).

**Botanical Name**: Clinopodium acinos  
**Family**: Lamiaceae  
**Part used**: Leaves and flowers

![Image](https://biointerfaceresearch.com/)

**Scheme 1.** The plant used in this paper and its family.

![Scheme 2](https://biointerfaceresearch.com/)

**Isopulegol**  
**Limonene**  
**Pulegone**  
**Retronecine**

**Scheme 2.** Main components in the used plant.

2.2.2. Solutions.

A corrosive solution of 1 M HCl was prepared to utilize double distilled water and standardized with Na₂CO₃. HCl solution prepared from a stock of HCl 37% (purchased from El-Nasr, Egypt) with water demineralized. The concentration of the extract used was (50, 100, 150, 200, 250, 300 ppm).

2.3. Techniques utilized for calculation of inhibition efficiency.

2.3.1. Weight loss technique (WL).

WL technique is a simple technique, which applied to calculate the inhibition efficiency of CA extract on MS in 1M HCl [7]. “Square pieces of C-S with size (2 cm x 2 cm x 0.2 cm) were used in this method. The MS pieces were prepared by using emery papers with a degree (600, 1000, 1200, 2000) then we use acetone to remove impurities from the surface. Inhibition of C-S corrosion was investigated under different temperatures (25, 30, 35, 40, 45) and various
concentrations of CA extract solution (50, 100, 150, 200, 250, 300 ppm). From this method, we can calculate corrosion rate (CR), surface coverage area (θ), and inhibition efficiency (% IE) as the next Eq. [8].

\[
\% \text{IE} = \theta \times 100 = [1 - (W/W^o)] \times 100
\]

Where, \( W^o \) and \( W \) are the MR, nonexistence, and existence, adding a deferent dose of investigating inhibitor continually.

2.3.2. Electrochemical techniques.

In Electrochemical studies, the % IE calculated by using three methods PP, EIS, EFM. These studies were achieved by using Gammy three-electrode cell at 25 °C. “The MS act as a working electrode, platinum electrode act as an auxiliary electrode, and a saturated calomel electrode act as a reference electrode. The working electrode was polisher with papers grit 1200 in size. Before tests, the electrode was inundation in HCl at potential natural for half hours. Until arrived at a steady-state”. All electrochemical measurements were performed utilizing a Gamry Instrument (PCI4/750) Potentiostat/ Galvanostat/ZRA.

2.3.2.1. PP technique.

In this method tafel curves obtained between 0.1 – 0.2 v with 1mVs\(^{-1}\) scan rate. All tests were done in freshly readying solutions at 25 °C. From the outcome data we can calculate % IE and θ as below [9]

\[
\% \text{IE} = 100 \times \theta = 100 \times [1 - (i_{corr(inh)} / i_{corr(free)})]
\]

\( i_{corr(inh)} \) and \( i_{corr(free)} \) are the current for corrosion in the nonexistence and existence of extract, continually.

2.3.2.2. EIS technique.

EIS tests carried out using AC signals of 5 mv at OCP in the frequency range (0.2Hz to 100 kHz). The diameters given of the capacitive loops improve in the existence of inhibitors and are led to the capacitive of the extent of inhibition of process corrosion, contrary to the lower of the \( C_{dl} \), which is given as:

\[
C_{dl} = 1/ (2 \pi f_{max} R_p)
\]

\( f_{max} \) = frequency maximum. The IE % and (θ) given from EIS analyses were obtained by the next relation:

\[
\% \text{IE} = 100 \times \theta = 100 \times [1 - (R_o^p/R_p)]
\]

\( R_o^p \) and \( R_p \) are the charge resistance in the nonexistence and existence of extract, respectively.

2.3.2.3. EFM technique.

The study of EFM was performed by using a signal with 10 mV amplitude with 2 single waves of 2 and 5 Hz [10]. The larger peaks were utilized to measure the (CF\(_2\) and CF\(_3\)) causality factors (\( \beta_c \) and \( \beta_a \)) and \( (i_{corr}) \) [11]. The inhibition of efficiencies % IE\(_{EFM} \) was calculated as follows:

\[
\% \text{IE}_{EFM} = 100 \times [1 - (i_{corr.} / i_o^p_{corr.})]
\]

Where, \( i_o^p_{corr.} \) and \( i_{corr.} \) are current corrosion in the nonexistence and existence of CA extract.
2.4. Surface analysis.

2.4.1. Atomic force microscopy.

AFM spectroscopy gives a 3D image of the film formed on the metal surface. This was achieved by Thermo Fisher Nicolet IS10, USA spectral range of 400 – 4000 cm\(^{-1}\). The image appears roughness, which gives information about the inhibitor reaction.

2.4.2. ATR-FTIR.

(FT-IR) spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). This spectrum gives a peak corresponding to the function group and explains the type of reaction.

2.4.3. X-ray photoelectron spectroscopy analysis (XPS).

The surface of MS after it engages in 1 M HCl solution in the absence and attendance of 300 ppm CA for 24 h was characterized by XPS K-ALPHA (Thermo Fisher Scientific, USA).

3. Results and Discussion

3.1. Weight loss (WL) tests.

As showed in the Fig (1), the “WL-time curves ” were determined in the presence and absence of various concentrations of CA extract. The values of CR, Θ, and IE% are listed in the Table (2). From the Table we noted that CR decrease with increasing of CA extract doses due to increasing of Θ by adsorption of CA extract on the MS surface. The IE% increase with increasing of CA extract doses and by increasing of temperature” [12].

![Figure 1](https://biointerfaceresearch.com/)
Table 2. WL measurements for MS at temperatures (25-45) at 120 min in the presence and absence of different doses of CA extract.

| Temp., °C | [inh], ppm | CR, mg cm⁻² min⁻¹ | Θ   | % IE |
|-----------|------------|---------------------|-----|------|
|           | Blank      |                     |     |      |
| 25        | 50         | 0.017               | 0.807 | 80.7 |
|           | 100        | 0.016               | 0.822 | 82.2 |
|           | 150        | 0.015               | 0.831 | 83.1 |
|           | 200        | 0.012               | 0.866 | 86.6 |
|           | 250        | 0.011               | 0.872 | 87.2 |
|           | 300        | 0.011               | 0.879 | 87.9 |
| 30        | Blank      | 0.119               | ---  | ---  |
|           | 50         | 0.022               | 0.817 | 81.7 |
|           | 100        | 0.020               | 0.833 | 83.3 |
|           | 150        | 0.018               | 0.851 | 85.1 |
|           | 200        | 0.013               | 0.889 | 88.9 |
|           | 250        | 0.013               | 0.893 | 89.3 |
|           | 300        | 0.012               | 0.899 | 89.9 |
| 35        | Blank      | 0.184               | ---  | ---  |
|           | 50         | 0.032               | 0.824 | 82.4 |
|           | 100        | 0.024               | 0.870 | 87.0 |
|           | 150        | 0.020               | 0.889 | 88.9 |
|           | 200        | 0.018               | 0.902 | 90.2 |
|           | 250        | 0.017               | 0.909 | 90.9 |
|           | 300        | 0.016               | 0.913 | 91.3 |
| 40        | Blank      | 0.211               | ---  | ---  |
|           | 50         | 0.034               | 0.837 | 83.7 |
|           | 100        | 0.021               | 0.899 | 89.9 |
|           | 150        | 0.020               | 0.907 | 90.7 |
|           | 200        | 0.017               | 0.918 | 91.8 |
|           | 250        | 0.016               | 0.922 | 92.2 |
|           | 300        | 0.015               | 0.928 | 92.8 |
| 45        | Blank      | 0.277               | ---  | ---  |
|           | 50         | 0.036               | 0.869 | 86.9 |
|           | 100        | 0.027               | 0.902 | 90.2 |
|           | 150        | 0.025               | 0.910 | 91.0 |
|           | 200        | 0.022               | 0.921 | 92.1 |
|           | 250        | 0.019               | 0.932 | 93.2 |
|           | 300        | 0.018               | 0.934 | 93.4 |

Figure 2. Plot of Langmuir adsorption of M-S in 1M HCl in the absence and presence of different doses of CA extract.

3.1.1. Adsorption isotherms.

The information of the interaction between CA extract and the MS surface in 1M HCl is given by adsorption isotherms. “There are several adsorption isotherms like Langmuir,
Temkin, Freundlich, Bockris-Swinkless, and Flory-Huggins isotherms [13]. But the Langmuir adsorption isotherm is the best fit that gives information on the interaction between the adsorbed layers of the CA extract and the surface of MS in 1M HCl and is represented by (Eq. 6). The relationship is linear among (C) and C/Ө given in lines straight (Fig. 2)’. K_{ads} belong to ΔG_{ads}^{0} as in (Eq. 7) [14].

\[
\frac{C}{Ө} = \frac{1}{K_{ads}} + C
\]

(6)

\[
ΔG_{ads}^{0} = RT \ln (K_{ads} \times 55.5)
\]

(7)

where K_{ads} = constant equilibrium, R = Universal gas constant, T = temperature in Kelvin and C = dose of CA extract.

From Vant Hoff equation:

\[
\ln K_{ads} = -\frac{ΔH^{0}}{RT} + \text{constant}
\]

(8)

By plotting ln K_{ads} vs. 1/T (Fig.3), gives a straight line with slope equals to ΔH^{0} as seen in Table 3.

![Figure 3. Plot of log K_{ads} vs 1/T for the adsorption of CA extracts on MS in 1M HCl at (25-45°C).](https://biointerfaceresearch.com/)

| Compound | T, K | k_{ads}x10^{-3}, M^{-1} | -ΔG_{ads}^{0}, kJ mol^{-1} | -ΔH_{ads}^{0}, kJ mol^{-1} | -ΔS_{ads}^{0}, J mol^{-1} K^{-1} |
|-----------|------|-------------------------|-----------------------------|-----------------------------|---------------------------------|
| CA        | 298  | 103                     | 21.5                        | 21.6                        | 144.6                           |
|           | 303  | 112                     | 22.0                        | 22.7                        | 143.9                           |
|           | 308  | 129                     | 22.7                        | 23.6                        | 144.0                           |
|           | 313  | 154                     | 23.6                        | 24.3                        | 144.3                           |
|           | 318  | 176                     | 24.3                        | 25.0                        | 144.4                           |

The data listed in Table (3) indicate that: 1) K_{ads} values increase with an increase in temperature. 2) ΔG_{ads}^{0} negative sign indicates that the CA extract is adsorbed spontaneously on M-S surface [15]. 3) ΔG_{ads}^{0} data more than 20 kJ mol^{-1}, which gives is a mixed type and spontaneous. 4) ΔH_{ads}^{0} negative sign indicates that the adsorption of CA extract is an exothermic process. 5. ΔS_{ads}^{0} have a negative sign because CA molecules freely moving in the bulk solution were adsorbed in an orderly fashion on to MS, resulting in a decrease in entropy [16].
3.1.2. Thermodynamic corrosion parameter.

The activation parameters for the corrosion of MS in 1M HCl in the presence and absence of various doses of CA extract are calculated from Arrhenius and transition state equations (Eq. 9, 10)

\[ k_{corr} = A e^{E_{a}^*/RT} \]  
\[ k_{corr} = \frac{RT}{Nh} e^{(\Delta S^*/R)} e^{(-\Delta H^*/RT)} \]

\( E_{a}^* \) = activation energy, As represented in (Figure 4) we plot log \( k_{corr} \) versus 1/T for MS in 1 M HCl in the presence and absence of various doses of CA extract than from the slope, the values of \( E_{a}^* \) were deliberate. In (Figure 5) we plot log \( k_{corr} / T \) versus 1/T, which gives a straight where the slope is \( \Delta H/2.303R \), and the intercepts are of log \( R/\text{Nh} + \Delta S^*/2.303 \) [17].

The obtained data are recorded in the (Table 4), and from it, we noted that:
1) \( E_{a}^* \) values in the presence of CA extract are higher than when CA is absent due to the adsorption of the CA on MS surface and formation of a barrier layer, which decreases CR. The values of \( E_{a}^* \) increase with increasing of CA dose. 2) \( \Delta S^* \) negative sign indicates that the activated complex at the rate-determining step favor an association rather than a dissociation [18].

![Figure 4. Plot of log \( k_{corr} \) vs 1/T for M-S in the presence and absence of CA extract in 1M HCl.](image1)

![Figure 5. Plot of log \( k_{corr} / T \) vs 1/T for MS in the presence and absence of CA extract in 1M HCl.](image2)
Table 4. Activation parameters for MS in presence and absence of CA extract in 1M HCl.

| Conc., ppm | $E^*$, kJ mol$^{-1}$ | $\Delta H^*$, kJ mol$^{-1}$ | $-\Delta S^*$, J mol$^{-1}$ K$^{-1}$ |
|------------|----------------------|-----------------------------|-----------------------------|
| Blank      | 36.2                 | 31.6                        | 169                         |
| 50         | 53.3                 | 50.7                        | 113                         |
| 100        | 53.5                 | 51.3                        | 114                         |
| 150        | 53.1                 | 50.3                        | 118                         |
| 200        | 53.4                 | 47.6                        | 128                         |
| 250        | 52.3                 | 48.7                        | 125                         |
| 300        | 52.2                 | 52.2                        | 115                         |

3.2. EFM measurements.

Figure 6 shows the current-frequency spectral chart obtained from EFM measurements in the absence and presence of various amounts of CA extract. From the chart, we can calculate Maximum peaks that were utilized to measure $i_{corr}$, $\beta_a$, $\beta_c$, and the causality factors (CF-2 and CF-3), which are listed in Table 5. The given data have shown that $i_{corr}$ decreases with an increase in CA extract doses, and the % IE increases by increasing the extract doses. The $\beta_a$, $\beta_c$ values indicate that the CA extract has not changed the corrosion mechanism. The values of CF-2 and CF-3 obtained from the chart are close to 2, and 3 of the theoretical values indicated that the obtained data are of good quality.

From Eq. 11, we can calculate % IE values, which rise by raising the CA extract doses [19].

\[
\%IE = 100 \times \left[1 - \left(\frac{i_{corr}}{i_{o, corr}}\right)^{\beta_c}\right]
\]

(11)

where $i_{o, corr}$ and $i_{corr}$ are current in the absence and presence of CA extract, respectively.

Figure 6. EFM data for MS in the absence and presence of different doses of CA extracts.
Table 5. EFM data for the corrosion of MS at various doses of CA extract at 25 °C.

| [inh.] ppm | $i_{corr}$, µAcm$^{-2}$ | $\beta_r$, mVdec$^{-1}$ | $\beta_a$, mVdec$^{-1}$ | CF-2 | CF-3 | C.R., mpy | $\Theta$ | %IE |
|------------|-----------------|-----------------|-----------------|-------|-------|-----------|--------|-----|
| 0.0        | 880             | 132.2           | 82.4            | 1.99  | 3.8   | 365.5     | -      | -   |
| 50         | 424.2           | 124.8           | 77.37           | 1.9   | 3.8   | 217.8     | 0.545  | 54.5 |
| 100        | 283.7           | 152.2           | 95.46           | 1.9   | 2.79  | 117.8     | 0.677  | 67.8 |
| 150        | 259.2           | 131.1           | 96.4            | 1.92  | 3.19  | 107.7     | 0.704  | 70.4 |
| 200        | 191.3           | 126.2           | 108             | 1.80  | 2.60  | 79.47     | 0.783  | 78.3 |
| 250        | 186.1           | 165.4           | 132.1           | 2.0   | 1.9   | 77.31     | 0.789  | 78.9 |
| 300        | 89.26           | 125.9           | 107.6           | 1.68  | 3.48  | 37.08     | 0.899  | 89.9 |

3.3. EIS method.

EIS is a useful method used to study the corrosion of MS in the absence and presence of various doses of CA extract in 1M HCl. Figs. (7, 8) show the Nyquist and Bode curves at the OCP at 25°C. Nyquist plots are characterized by semicircles loops at low frequencies. This method is represented simply in (Fig. 9) by Randle circuit. This circuit shows a parallel combination of which shows a parallel combination of a charge transfer resistance ($R_{ct}$) and the double-layer capacitance ($C_{dl}$), both in series with solution resistance ($R_s$)[20]. The corresponding $R_{ct}$ was also utilized to calculate IE and CPE, which is used to describe the double-layer [21]:

$$C_{dl} = Y_0 (2\pi f_{\text{max}})^{-n-1}$$

With 0 ≤ n ≤ 1, j = √-1 and $f_{\text{max}}$ is the frequency of the highest imaginary value, $Y_0$ is a frequency-independent constant, being defined as pure capacitance for n=1, resistance for n = 0, inductance for n = -1. The diffusion process is characterized by the value of n = 0.5. The value of (n) represents the deviation from the ideal behavior [40]. The values of n, $Y_0$, $R_{ct}$ charge transfer resistance, $C_{dl}$ double-layer capacitance, and the IE% were obtained and listed in (Table 6). The Nyquist plots obtained in the real system represent a general behavior where the double layer on the interface of MS/solution does not behave as an areal capacitor. The data obtained from the equivalent circuit are presented in Table 6. The data show that $R_{ct}$ values were increased by adding the extract. This is due to the formation of an insulating protective film at the metal/solution interface. Alternatively, $C_{dl}$ values were decreased due to a decrease in local dielectric constant and /or to an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface” [22]. The adsorption of the CA molecules on the MS surface lowered the electrical capacity due to they displace the water molecules, and the CA are originally adsorbed on the surface.

Figure 7. The Nyquist plots for MS in nonexistence and existence of various doses of CA extract at 25°C.
Figure 8. The Bode plots for the dissolution MS in nonexistence and existence of various doses of CA extract in 1M HCl at 25°C.

Figure 9. Equivalent circuit utilized to fit the EIS results.

Table 6. EIS value of MS in nonexistence and existence of various doses of CA extract at 25°C.

| [inh.] ppm | $Y_s$ ($\mu \Omega^{-1} cm^{-2} \times 10^6$) | $R_{ct}$ | n | $C_{dl}$ ($\mu F cm^{-2}$) | $\theta$ | %IE |
|------------|------------------------------------------|---------|-----|-------------------------|-------|------|
| 0.0        | 279.9                                    | 19.41   | 0.894 | 151                     | -     | -    |
| 50         | 204.9                                    | 62.15   | 0.875 | 100                     | 0.687 | 68.7 |
| 100        | 191.5                                    | 74.52   | 0.852 | 91                      | 0.739 | 73.9 |
| 150        | 171.5                                    | 76.84   | 0.858 | 84                      | 0.747 | 74.7 |
| 200        | 156.6                                    | 113.9   | 0.851 | 77                      | 0.822 | 82.2 |
| 250        | 155.2                                    | 144.6   | 0.811 | 64                      | 0.866 | 86.6 |
| 300        | 146.8                                    | 247.6   | 0.789 | 61                      | 0.922 | 92.2 |

3.4. PP tests.

PP measurements were carried out to study the effect of CA extract on the anodic and cathodic reactions occurring in the system. Figure 10 demonstrates the potentiodynamic polarization curves for mild steel without and with various doses of CA extract at 25°C.

The outcome electrochemical parameters are cathodic ($\beta_c$) and anodic ($\beta_a$) Tafel slopes, corrosion potential ($E_{corr}$), and corrosion current density ($i_{corr}$), which acquired and recorded in Table 7 [23]. From the outcome data, we noted that ($i_{corr}$) decrease with increasing of CA extract doses, but the ($\beta_a$, $\beta_c$) are approximately constant, and parallelled to the retardation of the 2 reactions were influence without exchanging the liquefaction mechanism [24]. Figure 10 showed that both cathodic and anodic reactions are inhibited, which indicated that CA extract is a mixed type inhibitor [25]. The appending of CA extract are exchange the $E_{corr}$ data in a negative direction. The (%IE) calculated from $i_{corr}$ reveals that the presence of various
concentrations of CA extract decreases the anodic and cathodic current densities and the polarization resistance.

![Figure 1](https://doi.org/10.33263/BRIAC112.97869803)

**Figure 10.** PP plots for the dissolution of MS in the presence and absence of various doses of CA extract.

| [inh.] ppm | -E<sub>corr</sub>, (mV vs. SCE) | R<sub>p</sub>, Ω | i<sub>corr</sub>, μA cm<sup>-2</sup> | β<sub>c</sub>, mV dec<sup>-1</sup> | β<sub>a</sub>, mV dec<sup>-1</sup> | C.R, mpy | Θ | % IE |
|------------|-------------------------------|----------------|----------------|----------------|----------------|-----------|-----|------|
| 0          | 304                           | 33             | 778            | 167            | 95             | 303       | -   | -    |
| 50         | 395                           | 66             | 356            | 150            | 84             | 148       | 0.542| 54.2 |
| 100        | 411                           | 146            | 157            | 149            | 82             | 65        | 0.798| 79.8 |
| 150        | 415                           | 166            | 135            | 137            | 83             | 57        | 0.826| 82.6 |
| 200        | 426                           | 211            | 115            | 136            | 95             | 48        | 0.852| 85.2 |
| 250        | 428                           | 221            | 98             | 126            | 83             | 41        | 0.874| 87.4 |
| 300        | 444                           | 346            | 56             | 115            | 73             | 25        | 0.928| 92.8 |

3.5. Surface characterization.

3.5.1. AFM study.

AFM is a useful method used to study the morphology of the MS surface. (Figs. 11-13) are 3D images for M-S polished surface in absence and presence of CA extract (300ppm) in 1M HCl for 24 hour at 25°C[26]. From the figures, we can see that: The surface is very clear for the free surface in the absence of CA extract and HCl, and the average roughness is 14.1 nm Figure (11); The surface more corroded in the absence of CA extract at 1M HCl, and the average roughness is 392.58nm Figure (12); The surface is less corroded in the presence of CA extract (300 ppm), and the average roughness is 212.9 nm Figure (13).

From the figures, we understand that: the roughness reduced in the presence of the inhibitor due to the formation of a protective film of CA extract on MS surface [27].

3.5.2. ATR-FTIR analysis.

In this method, we identify the adsorbed functional groups of CA extract adsorbed on the MS surface. “The mechanism of inhibition of corrosion of M-S by CA extract in HCl can be illustrated on the basis of molecular adsorption [28]. Chemical bonds in a molecule had been recognized by generating an infrared absorption spectrum. Functional groups and
characterizing covalent bonding information had been detected by FT-IR, which is an influential analytical device [29].

Figure 11. AFM 2D (a) and 3D (b) of MS free surface.

Figure 12. AFM 2D (a) and 3D (b) of MS electrodeposits in 1M HCl.

Figure 13. AFM images 2D (a) and 3D (b) of MS electrodeposits in the presence of CA extract.

Figure (14) signifies the ATR-IR spectrum of CA extract and the construction of the adsorbed film over the MS surface after immersion for 6 hr in 1 M HCl. FT-IR spectra of the CA extract stock (1000 ppm) and the spectra of MS surface after immersion in 1M HCl + 300 ppm of CA extract for 6 hours as compared to each other. From the compared spectra, we note that there are small shifts on the peak of some function groups, the absence of some functional
group, and some peaks not changed. These spectra are characteristic by OH group (3317 cm\(^{-1}\)– 3618 cm\(^{-1}\)) and carboxylate group at 1600cm\(^{-1}\). These shifts indicate that there is an interaction between MS and some of the inhibitor’s molecules”. The corrosion of MS inhibited after the addition of CA extract.

![Figure 14. ATR-FTIR spectra of CA stock solution (1000 ppm)(a) and adsorbed layer of CA on MS surface(b).](https://biointerfaceresearch.com/)

3.5.3. XPS.

X-ray photoelectron spectroscopy (XPS) analysis was performed to confirm the adsorption of the studied CA on the “MS surface and determine the chemical nature of the inhibitors/steel interface, and the results were discussed as below. The high-resolution XPS spectra survey obtained for M-S surface corroded in 0.1 M HCl solution in the presence of CA molecule is illustrated in Fig.15. All XPS spectra show complex forms, which were assigned to the corresponding species through a deconvolution fitting procedure. The binding energies (BE, eV) and the corresponding quantification (%) of each peak component are listed in Table 8. The high-resolution XPS spectra obtained for MS surface corroded in 0.1 M HCl composed of (Fe 2p, O 1s, Cl 2p, C 1s) as illustrated in Fig.16. While in the presence of the studied CA inhibitor, the XPS spectra consist of the same elements (Fe 2p, O 1s, Cl 2p, C 1s) in addition to N 1s core level, as shown in Fig.17. The XPS spectrum of Fe 2p shows six peaks. The high peak at lower binding energy (711.2 eV) corresponds to metallic iron [30]. The peak located at 714.6 eV is attributable to Fe 2p3/2, and the small peak at 719.40 eV corresponds to the satellite of Fe\(^{3+}\). In addition, the peaks at 724.3 eV and 727.9 eV can be attributed to Fe 2p1/2 due to the presence of iron in the form of Fe\(_2\)O\(_x\), \(\alpha\)-Fe\(_2\)O\(_3\), and FeOOH [31]. The last peak at 732.4 eV, which is related to the oxidation of the steel surface. The C 1s spectra of M-S in HCl alone and with the CA show two characteristic peaks at binding energy 284.6 eV and 286.2 eV assigned to a C–C bond and C=O bond, respectively, while in the case of CA only, there is more peak observed at 288.4 eV which is attributed to the sp\(^2\)-hybridized carbon, which comes from the inhibitor molecule. The XPS spectra of O 1s in blank solution shows three peaks, one of them at BE 530.0 eV, which is attributed to the Fe oxide (FeO and Fe\(_2\)O\(_3\)) [32]. The second one at a binding energy of 399.9 eV, this peak could be attributed to the neutral imine (-N=), and amine (-N-H) nitrogen atoms as previously reported [33]. According to the XPS results, the appearance peak of N in the protected sample surface spectra confirm adsorption of the studied CA inhibitor at the sample surface. Moreover, in the presence of the investigated
inhibitors”, it is clear that the O1s core level signal is significantly decreased, which is consistent with the adsorption of the CA on the M-S surface. All that confirms the adsorption of the investigated inhibitors on the MS surface in the HCl solution.

**Figure 15.** The XPS survey spectrum results of CA extract adsorbed on the MS in 1 M HCl at 25°C.

**Table. 8.** The binding energies (BE, eV) and the corresponding quantification (%) For CA extract.

| CA extract | Peak BE | FWHM eV | Area (P) CPS.eV | Atomic % |
|------------|---------|---------|----------------|----------|
| O1s        | 531.32  | 3.61    | 236337         | 40.37    |
| Fe2p       | 711.43  | 4.77    | 352512.4       | 12.18    |
| C1s        | 285.11  | 3       | 90437.76       | 39.44    |
| Cl2p       | 199.2   | 3.58    | 35415.26       | 6.49     |
| N1s        | 401.05  | 3.34    | 5913.11        | 1.52     |

**Figure 16.** High-resolution X-ray photoelectron deconvoluted profiles of (a) C 1s, (b) O 1s, (c) Cl 2p, and (d) Fe 2p for MS in 1 M HCl.
3.6. Mechanism of corrosion inhibition.

According to weight loss and electrochemical measurements, “the additions of CA extract leads to decrease the corrosion of MS. The outcome data showed that the mechanism of inhibition depends on the blocking of active sites of the MS surface by adsorption of CA extract. The adsorption of CA extract is carried by the adsorption of heteroatoms of the inhibitor, which are in different constituents of extract besides the availability of π- electrons in the aromatic system [34]. By phytochemical analysis, we know that: the CA extract many organic compounds. Temperatures study results showed that mechanical adsorption happens through physical adsorption. The MS surface, with its positive charge, prefers the adsorption
of Cl\(^{-}\) to produce a negative charge surface”. These molecules (CA extract) will be existing in the protonated form, so it can adsorb directly on the negative surface of MS [35] in an acidic medium by electrostatic attraction, as shown below. Schematic representation of the mode of adsorption of extract molecules on MS surface is shown in Fig. 18.

![Schematic representation of the mechanism of inhibition.](https://doi.org/10.33263/BRIAC112.97869803)

**Figure 18.** Schematic representation of the mechanism of inhibition.

4. Conclusions

The conclusions below are given according to the above results: CA extract is a good inhibitor used to decrease the corrosion of MS in HCl solutions; The outcomes data explained that: the inhibition efficiency increase by increasing the concentration of CA extract; When the plant extract is added, the double-layer, capacitances reduce, and charge travel resistance rises regardless of the blank solution; The adsorption of CA extract follows Langmuir adsorption isotherm; The result explained that the CA extract acts as a mixed-kind inhibitor; Techniques that are used to detect the corrosion inhibition process are MR, PP, EFM, and EIS are in reasonably good agreement; There is good agreement between chemical and electrochemical techniques.

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**Conflicts of Interest**

The authors declare no conflict of interest.

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