Analytical & Bioanalytical Electrochemistry

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Full Paper

Analysis of Fig Leaf Extract as Steel Eco-friendly Corrosion Inhibitor in Acidic Medium: Electrochemical, Gravimetric, Spectroscopic, and Surface Studies

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Received: 20 September 2023 / Received in revised form: 5 February 2024 / Accepted: 20 February 2024 / Published online: 29 February 2024

Abstract- The trend upwards using green, safe, and environmentally friendly corrosion inhibitors has led to many studies being conducted on plant extracts and presenting them as an ideal alternative candidate. Here, Fig leaf extract (FLE) was prepared quickly at a low temperature (313K) to preserve the main chemical composition and distilled water as the solvent of extraction. This green inhibitor was employed to prevent steel corrosion in hydrochloric acid 1 M. The inhibitory efficacy, adsorption, and action mechanism of this prepared inhibitor were assessed using potentiodynamic polarization, electrochemical impedance spectroscopy, and gravimetric measurements. Thermodynamic analysis and adsorption isotherms have been, also, applied to elucidate the adsorption mechanism. The obtained results have shown that FLE is of a mixed type, follows the Langmuir isotherm and his inhibitory efficiency reached a maximum of 94%. The formation of an inhibitor film chemically adsorbed was confirmed by the analysis of corrosion process activation parameters, and also by a rise in inhibition efficiency as temperature was increased. These findings were validated by FTIR and FTIR second derivative spectra. Steel surface morphology was investigated using SEM techniques and XRD analysis. A satisfactory corrosion inhibitory effect on acid steel was brought by fig leaf extract, which is in line with the desire for the use of environmentally friendly, non-toxic products.

Keywords- Green corrosion inhibition; Fig leaf extract; Electrochemical impedance spectroscopy; Weight loss; FTIR derivative spectra

1. INTRODUCTION

Multiple approaches have been employed for corrosion protection in science and engineering. Some of the common ones are material selection [1], electrochemical processes [2], coating deposition [3], and corrosion inhibitors [4]. Utilizing corrosion inhibitors, however, has been recognized as a good strategy for shielding metals from corrosion [5]. Acid solutions are frequently used in a variety of industrial operations, including petrochemical procedures, oil well stimulation, pickling, and acid cleaning. For these treatments to minimize metal degradation and dissolution, an inhibitor must be used [6,7]. Because of their many beneficial qualities, including their abundance in nature, renewable resources, low cost, and effective corrosion inhibition, using plant extracts as green inhibitors has gained a lot of interest [8,9]. These plant extracts are incredibly rich in compounds that are of interest, including phenolic acids, flavonoids, and furanocoumarins, as well as, minerals and vitamins. These species can bond to the metal using functional groups for a protective purpose against aggressive media [10-14]. Ficus carica is one of the richest sources of polyphenols and antioxidant molecules. Their leaves contain alkaloids, flavonoids, and tannins [15,16]. HPLC examinations indicated that fig leaves included phenolic acids, such as ferulic acid, 3-O-caffeoylquinic acid, and 5-Ocaffeoylquinic acid; flavonoids, such as quercetin 3-O-rutinoside and quercetin 3-Oglucoside; and furanocoumarins, such as psoralen and bergapten which could be an effective source for corrosion inhibition [17,18]. Fig leaves extract was used as a corrosion green inhibitor for zinc [19], aluminum [20], and brass [21] in acid media. For inhibition corrosion steel, alcoholic Ficus carica leaves extracts were used in different media such as petroleum medium [22], and 0.5 M sulfuric acid [23]. However, aqueous extract was employed in the corrosion inhibition of mild steel in a neutral medium (NaCl 3.5%) saturated with CO₂ [24] and in 2 M HCl [25].

The substitution of organic solvents like methanol, etc., is still necessary for reasons of health, the environment, and the economy. The easiest way to solve this conundrum, which has bothered government officials and business owners, is to use water as an extraction solvent. Aqueous extracts are also favored for their stronger bonding with metallic surfaces due to their higher polar phytochemical content [26].

Fig trees account for almost 10% of the country's arboreal heritage [27], and their leaves produce a substantial amount of agricultural waste. Because of their many beneficial qualities, including their abundance in nature, renewable resources, and low cost using fig leaves as a corrosion inhibitor presents a viable way to turn this waste into a useful resource and take care of environmental issues at the same time [28].

Herein, aqueous extracts from the leaves of *Ficus carica* (FLE) were employed as a green inhibitor against steel corrosion in an acid medium (1M HCl). Electrochemical impedance spectroscopy, potentiodynamic polarization curves, as well as the gravimetric method, were employed in the corrosion inhibition investigation. Thermodynamic and kinetics parameters

were also developed. For characterization, FTIR, FTIR Derivative, SEM tests, and XRD analysis were conducted.

2. MATERIALS AND METHODS

2.1. Extraction of Fig leaves

Fig leaves were harvested in a farm located around Guelma, Algeria. *Ficus carica* leaves were separated from the stalk rinsed thoroughly with tap water and left away to dry in a well-ventilated area shielded from sunlight. Three weeks later, the dry leaves were pulverized into a fine powder, using an electric grinder. Then, a mixture of Fig leaves powder and distilled water (10 g/100 mL) was put under stirring at 40 °C for 3 hours. After 30 minutes of ultrasonic treatment, the mixture was filtered. Finally, to use the recovered filtrate as a green inhibitor, it was put in a vial and kept in the refrigerator.

2.2. Preparation of steel samples

Corrosion tests were conducted on Mild steel (MS). Besides the iron which is the main component, MS contains other species which confer it its specific properties (Table S1). The mild steel plate was cut into a rectangular specimen (surface area of $1 \times 2 \text{ cm}^2$). The metal pieces were mechanically polished to a mirror-like finish. Finally, after a double cleaning with distilled water and ethanol, samples were dried and stored till use.

2.3. Preparation of the solution

1 M HCl, the corrosive solution, was prepared by using a 37% concentrated commercial hydrochloric acid solution. FLE was incorporated into the corrosive solution with different amounts of 0.05-0.25 V/V.

2.4. Electrochemical measurements

Electrochemical measurements were carried out using a potentiostat/galvanostat (VersaSTAT 3, Princeton Applied Research, AMETEK, USA). Potentiodynamic polarization curves and EIS tests were performed in a glass cell containing the electrolyte and the three conventional electrodes. Ag/AgCl (sat KCl) was the reference electrode while a Pt wire served as the auxiliary electrode. Steel samples were employed as the working electrode, and a 1 cm² part was exposed to the corrosive solution. Before starting the experiments, the electrodes were soaked in the corrosive solution to achieve steady values of the open circuit potential (OCP). The potentiodynamic polarization curves have been studied by scanning the potential from - 0.25 V to + 0.25 mV/E_{corr} with a 5 mV/s sweep rate. Electrochemical impedance spectroscopy (EIS) measurements were done using a frequency range of 10 kHz to 5 mHz and an amplitude

of 10 mV with 5 points per decade. Z-view software was used to analyze Nyquist and Bode data.

2.5. Weight loss method

The gravimetric tests were carried out in 1 M HCl with varying amounts of FLE extracts at five different temperatures (298, 308, 318, 328, and 338 K). A blank solution of 1 M HCl was also used to assess MS weight loss. The corrosion rate COR (mg/(cm².h)) and the inhibitory efficacy (IE) were evaluated following a four-hour immersion. IE% was calculated using the eq (1) and (2):

$$IE\% = \frac{COR - COR(FLE)}{COR} \times 100$$
(1)
$$COR = \frac{m_0 - m}{S \times t}$$
(2)

where COR and COR(FLE) are the calculated corrosion rates without and with the FLE inhibitor, respectively. m_0 and m are the mild steel samples weighed before and after immersion in the corrosive medium, respectively. S is the sample surface (cm²), and t is the immersion time (h). To obtain precise findings, each experiment was run in triplicate sets, and standard deviations were calculated.

2.6. FTIR spectra acquisition

A Perkin-Elmer Spectrum one spectrophotometer was used to collect FTIR spectra of fig leaves powder and the crashed layer formed at the steel surface. The wavenumber ranged from 4000 to 450 cm^{-1} with a resolution of 4 cm^{-1} .

2.7. Scanning electron microscope (SEM) and XRD Analysis

The morphology of the mild steel surfaces subjected to the corrosive solution without and containing 0.05 mL/mL FLE inhibitor was studied using a scanning electron microscope with energy dispersive spectroscopy SEM: TESCAN VEGA3. The formed layer on the mild steel surface for both uninhibited and inhibited acid solution was analyzed using an X-ray diffractometer (Rigaku Ultima IV diffractometer, using CuK α radiation ($\lambda = 0.15405$ nm). The obtained diffraction patterns were recorded in the 2 θ range of 10° to 90° with a scan rate of 5°/min.

3. RESULTS AND DISCUSSION

3.1. Electrochemical techniques

3.1.1. Open-circuit potential (OCP) measurements

Before EIS and polarization measurements, the mild steel potential variation was recorded versus an Ag/AgCl reference electrode in the blank solution, as well as in the electrolyte

containing FLE. The change in the open circuit potential (OCP) over time for MS in 1M HCl for the two media is represented in Figure 1. Apparently, OCP remains almost unchanged after five minutes of immersion, which indicates the achievement of a rapid steady state. Furthermore, it can be noted that with the incorporation of the inhibitor into the corrosive solution, the OCP tends to be shifted towards more positive values compared to the OCP of the blank. This means the metal becomes more noble in the presence of FLE. The OCP changes reflect an enhancement in the corrosion protection of MS when the FLE concentration rises. This might be the result of the formation of a protective layer on the steel surface which can further improve corrosion inhibition.



Figure 1. OCP plots of MS without and with various concentrations of FLE

3.1.2. Electrochemical impedance spectroscopy tests (EIS)

EIS is a precious tool in corrosion studies. It could bring many insights clarifying the steel/acid interface impedance parameters related to the addition of the inhibitor to the corrosive solution [29]. The FLE inhibitor amounts on the protective effect of MS were investigated. The findings are depicted in Figure 2 and Figure 3.

Figure 2 shows the Nyquist plot of the mild steel in HCl (1M) with and without different concentrations of FLE inhibitor. Nyquist plots exhibited depressed semicircles which may be due to the surface roughness, dislocation, or the adsorption of the FLE active species [30]. As reported elsewhere, the only one capacitive loop in Nyquist plots may suggest a one-time constant in relation to the charge transfer process [31]. It can be noted that as the FLE inhibitor concentration is increased, larger values of log |z| are observed at lower frequencies as illustrated in the Bode-modulus plots in Figure 3. It seems that FLE adsorbed on the MS surface was resistant to hydrochloric acid attack. A linear relationship (R²>0.99) was found between

log frequency and log |z| with a slope s (-0.74, -0.67). These values which are frequently noted in solid electrodes due to the interfacial impedance's frequency dispersion [32].



Figure 2. Electrochemical Nyquist plots for MS in the presence and absence of FLE at various concentrations



Figure 3. Bode and phase diagrams of FLE

As shown by Bode-phase plots in Figure 3, there is only one phase peak at middle frequencies, so only one time constant for EIS. This is depicted by a single constant phase element in the equivalent circuit which is related with the metal/solution interface [33]. All phase angles were greater than 0° and less than 90° . Additionally, it can be noted that the phase angles changed to more negative values when the inhibitor was incorporated to the corrosive solution. Further, the phase angle for the blank solution is roughly -60° , that angle rises to $(-65, -73^{\circ})$ for an inhibited solution. This outcome supports frequency dispersion once more

[34]. Greater peak heights observed at higher inhibitor amounts are indicative of a strong capacitance response [35].

A simple equivalent circuit, Figure 4, was built to model the impedance spectrum data. It is noteworthy to emphasize that surface flaws have an impact on the double-layer capacitance (C_{dl}) value.



Figure 4. Equivalent electrochemical circuit for EIS study adjustment

A constant phase element (CPE) simulates this effect [36]. The circuit was built taking into consideration the solution resistor R_s , the charge transfers resistor R_{ct} , and the constant-phase element CPE. The CPE can be expressed by the Eq. (3):

$$Z_{CPE} = Q^{-2}(j\omega)^{-n}$$
(3)

where Q is the CPE constant, j is the imaginary number, ω is the angular frequency in radians s⁻¹, n which refers to the degree of surface inhomogeneity or roughness of the surface which varies from 0 to 1. The CPE represents a resistance, inductor and capacitance if n is close to 0, -1 and +1, respectively. The double layer capacitance (Cdl) and the inhibition efficiency (IE_{EIS}%) were calculated using the following Eqs. (4) and (5) and gathered in Table 1.

$$C_{dl} = (QR_{ct}^{(1-n)})^{1/n}$$
(4)
$$IE_{EIS}\% = \frac{R_{ct}(FLE) - R_{ct}^{\circ}}{R_{ct}(FLE)} \times 100$$
(5)

 R_{ct}° is the charge transfer resistance without FLE and R_{ct} (FLE) is the charge transfer resistance when FLE is added to the corrosive solution. Table 1 shows a clear increase in the simulated charge transfer resistance (R_{ct}) with inhibitor amounts in the corrosive HCl solution. This feature reflects an increase in inhibition efficiency. This is confirming once again the existence of a protective inhibitor layer on the metal surface leading to a better stability of the metal in 1 M HCl solution containing FLE than in the blank solution. The values of n (0.75–0.79) are close to 1, further suggesting that the interface is capacitive [37,38]. This factor accounts for the surface's inhomogeneity [39] which is directly related to MS surface roughness, metal dissolution, the distribution of the active sites, and the adsorption of inhibitor molecules on the mild steel surface [40]. It is accepted that the lower surface roughness, the higher n value and vice versa.

 C_{dl} reflects the double layer between the corrosive solution and the charged mild steel surface. A decrease trend of the C_{dl} was observed with the increase of inhibitors' concentration. This could be explained by the replacement of the absorbed water molecules with large

dielectric constants by inhibitor molecules which have larger dimensions and lower dielectric constants [41]. According to Helmholtz model, given by Eq. (6) [42], the adsorption film on the metal surface thick with the increase of the concentration of corrosion inhibitor may be explained by the decreasing trend of C_{dl} . It is logical to infer that the molecules of inhibitor create a protective layer at the steel/solution interface:

$$C_{dl} = \frac{\varepsilon \times \varepsilon^{0}}{d} S \tag{6}$$

where ε is the dielectric constant of the protective layer, and ε^0 is the permittivity of free space $(8.854 \times 10^{-14} \text{ Fcm}^{-1})$ d is the thickness of the protective layer, and S is the exposed surface of the steel sample [43]. The relaxation time (τ) was calculated based on the C_{dl} values using the equation (7) [44, 45].

$$\tau = C_{dl} \times R_{ct} \tag{7}$$

From the calculated data, it can be stated that the obtained values of τ increase with a decrease in the C_{dl} values as different amounts of FLE are added. This indicates a reduction in the discharge and charge to the steel/solution interface. Moreover, the rise in the relaxation time constant according to the higher adsorption time which leads to the slow adsorption phenomenon, and the protective film becomes more stable [33]. The inhibition efficiency rises with the increase of FL extract amounts in the corrosive solution, varying from 90% to 94%.

Table 1. EIS parameters for MS in the absence and the presence of different concentrations of

 FLE

C (mL/mL)	R_{ct} ($\Omega.cm^2$)	$Q \times 10^{-4}$ (Ω^{-1} .cm ⁻	N	C _{dl} (µF.cm- ²)	-S	R ²	-α	τ (s)	IE* (%)
0.00	67 7	.8)	0.76	130	0.6720	0.0002	60 51	0.41	/
0.00	07.7	4.2401	0.70	139	0.0729	0.9992	00.51	9.41	/
0.05	670.1	1.6427	0.75	79	0.6893	0.9982	69.26	52.94	89.89
0.10	718.9	1.5986	0.76	81	0.7034	0.9985	70.84	58.23	90.58
0.15	778.5	1.5797	0.75	79	0.6884	0.9982	72.81	61.50	91.30
0.20	1037	1.2448	0.76	65	0.6884	0.9982	65.74	67.40	93.47
0.25	1214	1.0229	0.79	59	0.7408	0.999	73.30	71.63	94.42

*mean value and all standard deviations < 2

3.1.3. Potentiodynamic Polarization tests

Potentiodynamic polarization analysis was used to study the resistance to corrosion of mild steel in the HCl (1 M) medium in the presence and absence of FLE at different concentrations. The resulting data are shown as polarization curves (Figure 5). The extrapolation approach was used to determine the values for the corrosion current density (icorr), corrosion potential (Ecorr),

cathodic and anodic Tafel slopes (βc and βa), polarization resistance and inhibition efficacy (IEp%) for five different concentrations of FLE in 1M HCl medium regrouped in Table 2. Inhibition efficacy (IEp%) and polarization resistance (R_p) were calculated using the following eq (8) and eq (9), respectively:

$$IE_P\% = \frac{i^\circ_{corr} - i_{corr}}{i^\circ_{corr}} \times 100$$
(8)

where i°_{corr} and i_{corr} are the corrosion current densities in 1M HCl solutions without and with the extracts.

$$R_p = \frac{\beta a \times \beta c}{2.303 \times i_{corr} \times (\beta a + \beta c)}$$
(9)



Figure 5. Potentiodynamic polarization curves of steel in the presence and absence of different concentrations of FLE

Figure 5 illustrates that the addition of FLE causes a decrease in the cathodic and anodic current densities, with inhibitory efficiency reaching a maximum of 88.35%, in the presence of 0.05 mL/mL of FLEs. Demonstrating a decrease in MS anodic dissolution and a delay in the cathodic hydrogen evolution reaction. Furthermore, the results indicate that FLE fall under the category of mixed-type inhibitors because the shift in E_{cor} value was less than 85 mV [46-48]. When FLE is incorporated to the corrosive solution, the cathodic Tafel lines' (βc) slope values vary, reflecting the impact of the extract on the kinetics of the cathodic mechanism. Moreover, the values of βc and βa exhibit an uneven pattern, indicating that mechanisms other than adsorption, are involved in the inhibition of corrosion such as the presence of species/anions in the solution [49,50]. Moreover, Rp values were found to increase in the presence of FLE. According to these two occurrences of decreasing icorr and raising Rp suggest that the FLE is

probably responsible for producing a robust barrier that shields the metal surface from corrosion. The EIS results support the polarization measurements.

С	E _{corr}	I _{corr} *	-βc	βa	$R_p(\Omega.cm^2)$	$IE_{Rp}*$	IE _p *
(mL/mL)	(V vs	(A.cm ⁻²)	$(V.dec^{-1})$	$(V.dec^{-1})$		(%)	(%)
	Ag/AgCl)						
0.00	-0.4009	2.9129×10 ⁻⁴	0.1121	0.0639	60.67		/
0.05	-0.3926	3.3928×10 ⁻⁵	0.1694	0.0642	595.82	89.81	88.35
0.10	-0.3926	7.9401×10 ⁻⁵	0.1803	0.0596	244.96	75.23	72.74
0.15	-0.4004	6.1424×10 ⁻⁵	0.1803	0.0758	377.27	83.91	78.91
0.20	-0.3830	3.6000×10 ⁻⁵	0.1641	0.0580	516.88	88.26	87.64
0.25	-0.3908	4.8645×10 ⁻⁵	0.1745	0.0684	438.67	86.16	83.30

Table 2. Tafel parameters for MS without and with different concentrations of FLE

*mean value and all standard deviations < 1.5

3.2. Weight loss measurements

The time period the steel is exposed to the corrosive media has a major impact on the rate of corrosion. So, different steel immersion times in 1 M HCl, including 1, 2, 3, 4, 5 and 6 hours were investigated. The rate of metal corrosion in hydrochloric acid (1 M) increases over time and reaches a maximum value after 4 hours. This shows that corrosion peaks after 4 hours of exposure. To explore the temperature and concentration of FLE effects on weight loss, this time period was employed as an immersion duration.

3.2.1. Effect of temperature

The corrosion rate COR (mg/(cm².h)) and the inhibitory efficacy (IE) were evaluated following a four-hour immersion and regrouped in Table S2 and S3. The results reported in Figure 6 indicate that raising the temperature and adding different FLE concentrations improve inhibitory effectiveness and slow down steel corrosion. The inhibitor efficiency reached a maximum of 90.16% at (T=338K, C=0.25mL/mL). The persistent layer that was formed on the surface of steel as a result of a chemical adsorption (the IE% increased with increasing temperature) is thought to be responsible for this behaviour. This layer protects steel from the severe attack of hydrochloric acid and slows the metal dissolving. Inhibition efficacies obtained from EIS and polarization curves were a little above those obtained from weight loss. This discrepancy could be ascribed to the fact that weight loss reflects the mean corrosion rate for a long period of immersion, while electrochemical procedure measures the instant electrochemical corrosion parameters [51].



Figure 6. Inhibitory efficiency as a function of FLE concentrations at various temperatures

The relationship between temperature and corrosion rate was illustrated by the Arrhenius equation. The corrosion process activation parameters were estimated following eq. (10): E_a

$$\log CR = \log A - \frac{Ea}{2.303 \text{ RT}}$$
 (10)

where, E_a , and A are the activation energy, and the pre-exponential factor, respectively while R and T have their usual meaning. Ea can be calculated from the slope of the plot of log (CR) *vs.* 1/T (Figure 7). In Table 3, the activation energy of the corrosion process in HCl without an inhibitor is calculated to be 60.83 kJ.mol⁻¹, which is close to the value given by Cherrak *et al.* [52].



Figure 7. The Arrhenius plot with and without various FLE concentration

Additionally, it appears that the activation energies (E_a), where the inhibitor is added to HCl corrosive solution, are lower than those obtained in the blank solution, indicating that the inhibitory activity of FLE molecules on the surface of the steel likely followed a process of chemical adsorption, as it was reported by several authors [53-56]. The formation of an inhibitor film chemically adsorbed was confirmed by an increase in inhibition efficacy with a rise in temperature [54,55].

The activation enthalpy (ΔH_a) and the activation entropy (ΔS_a) of the system can be calculated from the transition state equation (11).

$$\log\left[\frac{CR}{T}\right] = \log\left[\frac{R}{N_{A}h}\right] + \frac{\Delta Sa}{2.303R} - \frac{\Delta Ha}{2.303RT}$$
(11)

N_A is the Avogadro's number and h is the Planck's constant. The plot of log (CR/T) *vs.* 1/T is shown in Figure 8 and the values for (Δ H_a) and (Δ S_a) are derived from the slopes and intercepts, respectively (Table 3). The steel dissolution process is endothermic, which implies that mild steel is harder to dissolve, according to the positive values of the enthalpies Δ H_a [56]. There is less disorder between the reactants and the activated complex when there are negative entropy values, which show that the activated complex in the rate-determining phase is an association step rather than a dissociation step [57].



Figure 8. Transition state plots for MS in 1 M HCl without and with various FLE concentrations

Since the values of E_a are greater than the corresponding values of ΔH_a , corrosion should entail a gaseous reaction, specifically the hydrogen evolution reaction, that is accompanied by a diminution in the overall reaction volume [58]. In this case, $E_a - \Delta H_a$ value may clarify the involved phenomenon. For FLE, the ($E_a-\Delta H_a$) value is 2.62 kJ/mol, which is almost equivalent to the $R \times T$ average. The corrosion process is therefore stated to be a unimolecular reaction, depicted by the following eq. (12) [59]:

$$Ea - \Delta Ha = R \times T \tag{12}$$

Table 3. Activation parameters for mild steel in 1 M HCl without and with various concentrations of FLE

C (mL/mL)	Ea (kJ.mol ⁻¹)	ΔHa (kJ.mol ⁻¹)	Ea-∆Ha	-ΔSa (J.mol ⁻¹ . K ⁻¹)
0.00	60.83	58.21	2.62	66.49
0.05	28.81	26.19	2.62	75.17
0.10	32.54	29.92	2.62	168.77
0.15	52.58	49.96	2.62	107.45
0.20	23.12	20.50	2.62	195.53
0.25	33.99	31.37	2.62	166.22

3.2.2. Adsorption isotherm

To evaluate the equilibrium constant Kads, a number of isotherms, including Langmuir, Temkin, Freundlich, and Frumkin, were examined. These isotherms parameters were determined through the linearized form and their slopes and intercepts values, along with the respective correlation coefficients are regrouped in the supplementary material (Table S4).

The Langmuir adsorption isotherm represented in Figure 9 was found to be the best-fit isotherm through the respective correlation coefficients.



Figure 9. Calculated Langmuir isotherms using gravimetric measurements of FLE at various temperatures

For different temperatures (298, 308, 318, 328, and 338 K), plotting (C_i / θ) vs. (C_i) results in straight lines with a coefficient of determination near to unity. The equilibrium constant was calculated using the line's intercept in Figure 9. It can be noted that FLE molecules were strongly adsorbed on the metal surface, as evidenced by the rise in Kads values with rising temperature [60] (Figure 10). Herein, the obtained Langmuir adsorption coefficients cannot be used to calculate Gibbs free energy and enthalpy change in the adsorption processes for the plant extracts whose composition and/or content are undefined [61]. The intermolecular synergy of the various components in natural extracts is typically used to explain the inhibitory action.



Figure 10. Kads versus temperature plot for FLE

3.3. FTIR spectroscopy

FTIR spectra were acquired to distinguish the various functional groups and types of bonds in the powder of FLP and the film formed on the metal surface for the extract Fe-FLE. Figure 11 displays the FTIR spectra and the inset comprises the second derivative spectra for comparison purposes. In FLP, Hydroxyl groups (O-H) appear at 3373 cm⁻¹. This broadband could be hiding another band attributed to the N-H groups of alkaloids widely found in leaf extract [62]. Two bands at 2917 and 2849 cm⁻¹ are due to symmetric and asymmetric CH stretching vibrations (vCH, alkyl). The adsorption bands between at 2350-2300 cm⁻¹are ascribed to C \equiv N stretching vibrations. The 1760–1500 cm⁻¹ region corresponds to C=O of esters, acids and carboxylate and C=C stretching vibrations of the aromatic ring. The bands between 1200 and 1100 cm⁻¹ are attributable to C–O and C–N stretching vibrations as well as OH deformation vibrations. The strong bands between 1150 and 1000 cm⁻¹ were mostly the result of the endocyclic and exocyclic C–O stretching vibrations of carbohydrates [63]. From spectra (Figure 11), we can discern similarities in the FTIR spectra of powder and the scraped film, demonstrating that the extract has been adsorbed on the steel surface. A second derivative treatment of the spectra was utilized to highlight and analyze variations between the spectra of powdered leaves and the film produced on surface steel.



Figure 11. FTIR spectra of FLP and Fe-FLE adsorbed on mild steel. In the inset the second derivative spectra

The peaks in the second derivative mode are sharper and more bands are resolved than in conventional spectra, as seen in Figure 11 (inset). The second derivative of the FTIR spectra of the powder and the film formed at the steel surface revealed significant differences and showed a shift in the bands assigned to the N-H, O-H, C-O, C=O, C=C, C-N and C=N groups, confirming the adsorption of the protective layer formed due to interactions between these functional groups and the active sites of the metal surface. The adsorption of the FLE species on the steel surface was previously demonstrated electrochemical measurement techniques. These findings are supported by FTIR and FTIR second derivative.

3.4. Scanning electron microscope (SEM) results

Metal surfaces can be examined using scanning electron microscopy. The SEM images depict the steel surface after being soaked for 4 hours in both inhibited and uninhibited 1 M hydrochloric acid solutions. As a result of an aggressive attack by HCl in the absence of inhibitors. Figure 12a shows a highly damaged surface. It is highly affected by the presence of micro cracks and micro cavities. SEM observations in the presence of FLE (Figure 12b) demonstrate that the surface becomes smoother and the formation of an inhibitory layer leads to the blocking of the corrosive medium attack.



Figure 12. SEM morphologies of the soaked MS in 1M HCl solutions (a) without FLE inhibitor, (b) with FLE inhibitor

3.5. XRD results

To ascertain the crystal structure of the molecules formed on the metal surface submerged in the corrosive medium (1M HCl) in the presence and absence FLE, X-ray diffraction analysis was carried out Figure 13. All information related to these crystal structures (formula, hkl, crystal system, percentage, and reference) corresponding to each peak was identified using the Panalytical X'Pert High Score program. The diagrams obtained in the absence (Figure 13a) and in the presence of FLE (Figure 13b) show a cubic iron peak (ref. code:01-087-0721) at $2\theta =$ 44.7° (1 1 0), 64.9° (2 0 0) and 82.3° (2 1 1) [63].



Figure 13. XRD pattern of the mild steel immersed in 1 M HCl solutions (a) without FLE, (b) with FLE

The characteristic peaks at $2\theta = 19.7^{\circ} (2 \ 1 \ 2), 22.7^{\circ} (1 \ 1 \ 0)$ and $40.2^{\circ} (2 \ 0 \ 0)$ corresponding to an orthorhombic iron oxide (Fe₃O₄, ref. code: 01-076-0958), a hexagonal iron chlorate hydrate (Fe(ClO₄)₂(H₂O)₆, ref. code: 01.083.1493) and a cubic iron oxide FeO (ref. code: 01-

079-1972), respectively, are observed only on the diagram of the uninhibited solution and disappear for the diagram of the inhibited solution. Due to the presence of an organic molecule, an amorphous peaks appear at $2\theta = 8.07^{\circ}$ for FLE, these observations demonstrate that the metal's oxidation reaction is inhibited and that a protective film has been formed on the surface of steel.

3.6. A brief comparative study

Recently, scientific research has focused on investigating low-cost inhibitors, more effective and environmentally friendly. Table 4 provides a comparison of the FLE performances as corrosion inhibitor in different media. It can be stated that a very High inhibitory efficiency was achieved (exceeds 94%) for fig leaves extract. This inhibitory efficiency is almost greater than that was reported by previous works. Furthermore, FLE was quickly prepared at a low temperature (313K) and using only distilled water.

FLE / Corrosion medium	Solvent/ Temperature	Type of adsorption/ Isotherm	Method	IE%	Ref.
Petroleum Medium	Ethanol / 45°C	Physisorption / Langmuir	Polarization	80	[22]
0.5 M H ₂ SO ₄	Ethanol / -	Chemisorption / Temkin	Weight loss, Polarization, EIS, EFM, FTIR and AFM	95.7	[23]
3.5wt% NaCl solution saturated with CO ₂	Bidistilled water / 80 °C	Physisorption / Langmuir	Polarization, EIS, SEM, FTIR and Molecular dynamics	90	[24]
2 M HCl	Bidistilled water / 100°C	Physisorption / Langmuir	Weight loss, Polarization and EIS	87	[25]
1 M HCl	Distilled water / 40°C	Chemisorption / Langmuir	EIS Polarization Weight loss, FTIR, FTIR derivative, SEM and XRD	94	This Work

Table 4 Comparison of FLE extract for steel results obtained in the present study with other previous studies

A comparison of inhibition efficiency of FLE with aqueous plant extracts on steel in 1M HCl was given in Table 5. The result obtained in this study compared well with some plant extracts that have been applied as steel inhibitors in acid medium.

Plant extract	IE (%)	Ref.
Citrullus lanatus fruit extract	90	[64]
Green Eucalyptus leaf extract	88	[65]
Olive leave extract	93	[5]
Fig Leaves Extract	94	This study

Table 5. Comparison of inhibition efficiency of FLE extract for steel with other aqueous plant

 extracts

4. CONCLUSION

This study established the ability of FLE to act as an effective green corrosion inhibitor. The addition of FLE leads to a rise in the charge transfer resistance (R_{ct}) and a decrease in the double-layer capacitance (C_{dl}). The mixed character of this inhibitor was confirmed by the potentiodynamic polarization curves. The gravimetric method findings showed that the chemical adsorption is validated by the increase in IE% with increasing temperature and the values of E_a obtained when Fig leaf extract was added to the corrosive solution were lower compared to the HCl solution which further support the proposed chemical adsorption phenomenon.

FLE adsorption obeys to the Langmuir model. The obtained results using EIS techniques, electrochemical polarization and weight loss tests were in good agreement. FTIR and FTIR derivative analysis revealed the existence of various functional groups (N-H, O-H, C-O, C=O, C=C, C-N and C=N) that are responsible for the adsorption of the FLE molecules. SEM and XRD analysis proved that an inhibitory layer has been formed on the metal surface.

Finally, this natural extract is in keeping with the desire for green, non-toxic, and environmental protection and have a satisfactory inhibitory impact on acid steel corrosion.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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