

Corrosion inhibition of mild steel by Fennel seeds (*Foeniculum vulgare* Mill) essential oil in 1 M hydrochloric acid solution

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Abstract

As the importance of environmental protection has become increasingly recognized, the development of new green corrosion inhibitors has received increasing attention. In the present work, the corrosion inhibition ability of essential oil of Fennel seeds (EOF_s) on the mild steel (MS) in 1.0 M HCl was evaluated by using different chemical and electrochemical methods such as: weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) methods at various temperatures. Potentiodynamic polarization curves showed that EOF_s acts essentially as a mixed-type inhibitor controlling cathodic and anodic reactions, and the inhibition efficiency of up to 88% at 2 g/L was obtained. The EIS results showed an increase in polarization resistance (R_p) while the double layer capacitance (C_{dl}) decreases with an increase in EOF_s concentrations. Weight loss analysis proved 89% inhibition efficiency for the acid solution containing 2 g/L of EOF_s. The obtained results also showed that the inhibition efficiency decreased with an increase in the temperature, and the efficiencies of 89, 86, 80, and 76% were obtained at 303, 313, 323, and 333 K, respectively. The activation energy (E_a) of the corrosion process is 2.60 kJ/mol, the enthalpy (ΔH_a^*) is 79.95 kJ/mol and the entropy (ΔS_a^*) is 1.4 J·mol⁻¹·K⁻¹.

Keywords: corrosion inhibition, mild steel, HCl, EIS, PDP, Fennel, Langmuir isotherm.

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Introduction

Acid solutions are widely used in industry for several processes such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [1, 2]. During the past decade, many techniques have been used to minimize the corrosion of iron due to attack by acids. One of the techniques for minimizing corrosion is the use of inhibitors [3–5]. Most of the corrosion inhibitors are organic compounds having heteroatoms in their aromatic ring (N, S, O, P) or long-chain carbon [6–19].

Most of the synthetic chemicals are toxic to the environment. Due to the toxicity of some corrosion inhibitors, the search for green corrosion inhibitors has been increasing. Most of the natural inhibitors are environmentally friendly, non-toxic, and biodegradable [20–23].

Fennel is a small genus of annual, biennial or perennial herbs distributed in central Europe and in the Mediterranean region. It is widely cultivated throughout the temperate and tropical regions of the world for its aromatic fruits, which are used as a culinary spice [24]. Mature fennel fruit and its essential oil are used as flavoring agents in food products such as liqueurs, bread, pickles, pastries, and cheese. They are also used as a constituent in cosmetic and pharmaceutical products [25]. There have been several reports on fennel oils, including reports on various biological activities of the essential oil, such as hepatoprotective effect [26], antioxidant activity [27], antithrombotic activity [28], anti-inflammatory activity [29], antidiabetic activity [30], antitumour activity [31] and acaricidal activity [32].

In the present work, the corrosion inhibition effect of mild steel (MS) in 1 M HCl by essential oil of fennel seed was investigated using weight loss, potentiodynamic polarization methods and electrochemical impedance spectroscopy (EIS).

1. Experimental details

1.1. Material plant and extraction

Dried Fennel seeds were collected from the region of Meknes (north of Morocco) in June 2015 and were subjected to hydrodistillation in the Clevenger type device for 4 hours.

1.2. Isolation of essential oil

The essential oil of fennel seeds was dried oven anhydrous Na_2SO_4 and stored in dark glass at 4°C until analysis.

1.3. Electrodes and chemical and test solution

The corrosion tests have been performed, using the gravimetric and electrochemical measurements, on electrodes cut from sheets of carbon steel with the chemical composition: 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu, and the remainder iron (Fe). The aggressive medium

of 1 M HCl used for all studies was prepared by dilution of analytical grade 37% HCl with double distilled water. The inhibitor was dissolved in an acid solution at the required concentrations (in g/L), and the solution in the absence of inhibitor was taken as blank for comparison purposes. The concentrations of Essential oil of fennel seed (EOF_s) used in this investigation were varied from 0.5 to 2 g/L.

1.4. Weight loss measurements

The gravimetric measurements were realized in a double-walled glass cell equipped with a thermostat-cooling condenser. The mild steel specimens used have a rectangular form with a dimension of 2.5×2.0×0.2 cm was abraded with a different grade of emery paper (320–800–1200) and then washed thoroughly with distilled water and acetone. After weighing accurately, the specimens were immersed in beakers which contained 100 ml acid solutions without and with various concentrations of EOF_s at temperature the 303 K remained by a water thermostat for 6 h as immersion time. The gravimetric tests were performed in triplicate at the same conditions. The corrosion rates (C_R) and the inhibition efficiency (η_w , %) of mild steel have been evaluated from mass loss measurement using the following equations:

$$\eta_w = \frac{C_R - C'_R}{C_R} \quad (1)$$

$$\theta = 1 - \frac{C'_R}{C_R} \Rightarrow \theta = \frac{(\eta_w \%)}{100} \quad (2)$$

Where C_R and C'_R are the corrosion rates of the mild steel in 1 M HCl without and with the studied range of the EOF_s concentrations, respectively, θ is the degree of surface coverage.

1.5. Electrochemical measurements

Electrochemical measurements, including stationary methods (PDP) and transient (EIS), were performed in a three-electrode cell. Pure mild steel specimen was used as the working electrode; saturated calomel (SCE) as a reference and area platinum as a counter electrode (CE) were used. All potentials were measured against SCE. The working electrode was immersed in a test solution for 30 min until the corrosion potential of the equilibrium state (E_{corr}) was achieved using a type of PGZ100 potentiostat. The potentiodynamic polarization curves were determined by a constant sweep rate of 1 mV/s. The measurements of the transitory method (EIS) were determined; using ac signals of amplitude 10 mV peak to peak at different conditions in the frequency range of 100 kHz to 10 MHz. The data obtained by the EIS method were analyzed and fitted using graphing and analyzing impedance software, version *Zview2*. For PDP method, the inhibition efficiency of the studied compound was calculated using the following equation:

$$\eta_{\text{PDP}}(\%) = \left[1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right] \times 100 \quad (3)$$

Where i_{corr} and i_{corr}^0 are the corrosion rates in the presence and absence of inhibitor, respectively. The impedance diagrams were determined by the EIS method. To confirm reproducibility, all experiments were repeated three times and the evaluated inaccuracy does not exceed 10%. For EIS method, the inhibition efficiency was calculated using the following equation:

$$\eta_{\text{EIS}}(\%) = \left[\frac{R_{\text{p(inh)}} - R_{\text{p}}}{R_{\text{p(inh)}}} \right] \quad (4)$$

Where R_{p} and $R_{\text{p(inh)}}$ were the polarisation resistance of mild steel electrode in the uninhibited and inhibited solutions, respectively.

2. Results and discussion

2.1. Polarization results

The polarization plots recorded in the PDP experiments on MS in the studied medium (1.0 M HCl) in the blank solution and with different concentrations of EOF_s at 303 K are shown in Figure 1. The PDP parameters, the corrosion current densities (i_{corr}), the corrosion potential (E_{corr}), the cathodic Tafel slope (β_{c}) and corrosion inhibition efficiencies η_{PDP} (%) were calculated and presented in Table 1.

Figure 1 shows that the addition of EOF_s to acid media affected the reaction of cathodic and anodic branches as shown in PDP curves. The inhibitor causes the reduction of the MS dissolution, as well as retards of the hydrogen evolution reaction which indicates the mixed type of tested Fennel essential oil [33, 34]. Further inspection of results reveals that both anodic and cathodic slopes are approximately constant. Based on the data, we can suggest that the inhibiting action of our compound is based on a purely blocking mechanism [35]. Thus, all the calculations in our study were based on this assumption.

Table 1. The electrochemical parameters calculated by the PDP technique for the corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of EOF_s at 303 K.

Inhibitor	Conc. (g/L)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_{\text{c}}$ (mV·dec ⁻¹)	β_{a} (mV·dec ⁻¹)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	η (%)
Blank	–	496.0	162	113	564.0	–
EOF _s	0.5	498	165	115	197	65
	1.0	494	161	111	118	79
	1.5	497	169	114	91	83
	2.0	496	167	113	69	88

Results summarized in Table 1 indicate that with the addition of inhibitor to studied medium, the i_{corr} were significantly reduced and became only $69 \mu\text{A}/\text{cm}^2$. Meanwhile, η_{PDP} (%) of the studied fennel oil increase significantly with the increase in EOF_s concentration. Therefore, EOF_s can protect efficiently the MS dissolution in 1 M HCl solution.

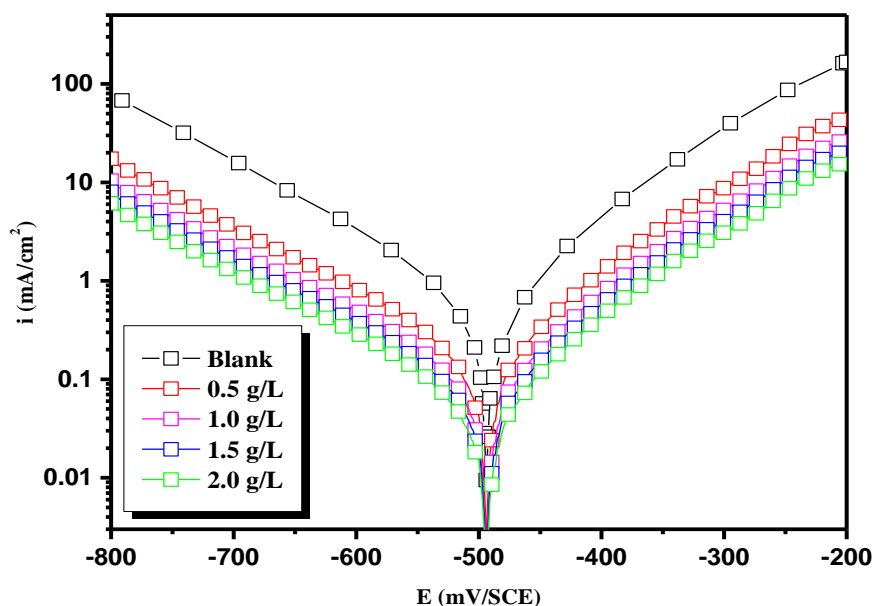


Figure 1. Potentiodynamic polarization curves for mild steel in 1 M HCl solution in the presence and absence of different concentrations of EOF_s at 303 K.

2.2. Electrochemical impedance spectroscopy (EIS)

Figure 2 shows Nyquist plots for mild steel in 1 M HCl in the absence and presence of different concentrations of EOF_s in the tested concentration range at 303 K. Nyquist plots consist of one capacitive loop with one time constant. In Figure 2, one single capacitive loop in the high-frequency range observed in all diagrams, this attributed to the charge transfer process. From the same figure, we can see that capacitive loops in this medium are not perfect semicircles. This phenomenon can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of the electrode surface [36, 37]. The direct relationship between the capacitive loop diameter and the EOF_s inhibitor concentration can be attributed to the increase in the polarization resistance (R_p) as a result of increasing the surface coverage of the corrosion inhibitor [38]. Consequently, the η_{EIS} (%) value is expected to increase as the concentration of the inhibitor is increased, exactly as is found and shown in Table 2.

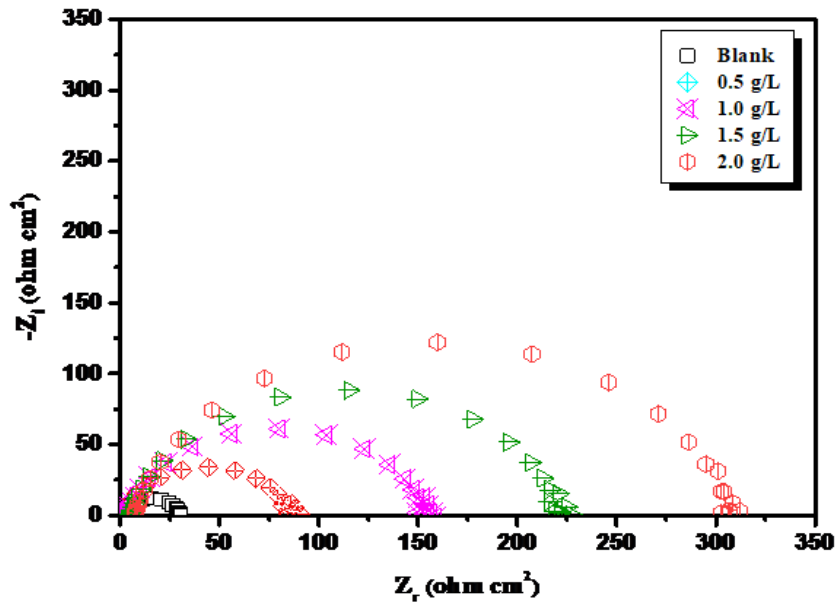


Figure 2. Nyquist plots for carbon steel in 1 M HCl solution containing various concentrations of EOF_s at 303 K.

The impedance spectra were fitted to the R_s (R_{ct} CPE) equivalent circuit of the form in Figure 3. In this circuit, R_s is the solution resistance, R_{ct} denotes the charge-transfer resistance and CPE is the constant phase element. The introduction of CPE into the circuit was necessitated to explain the depression of the capacitance semicircle, which corresponds to surface heterogeneity resulting from surface roughness, impurities, and adsorption of inhibitors [39]. The impedance of this element is frequency-dependent and can be calculated using the equation [40]:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^n} \quad (5)$$

Where Q is the CPE constant (in $\Omega^{-1} \cdot \text{S}^n \cdot \text{cm}^{-2}$), ω is the angular frequency (in $\text{rad} \cdot \text{s}^{-1}$), $j^2 = -1$ is the imaginary number and n is a CPE exponent which can be used as a gauge for the heterogeneity or roughness of the surface [41, 42]. In addition, the double layer capacitances, C_{dl} , for a circuit including a CPE were calculated by using the following Equation 6:

$$C_{dl} = \sqrt{Q \times R_p^{1-n}} \quad (6)$$

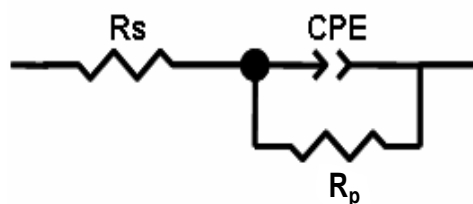


Figure 3. Equivalent electrical circuit.

Table 2. Impedance parameters recorded for mild steel electrode in 1 M HCl solution in the absence and presence of different concentrations of inhibitor at 298 K.

Inhibitor	Conc. (g/L)	R_{ct} ($\Omega \cdot \text{cm}^2$)	N	$Q \cdot 10^{-4}$ ($\text{s}^n \cdot \Omega^{-1} \cdot \text{cm}^{-2}$)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	η_{EIS} (%)
Blank	–	29.35	0.91	1.7610	91.63	–
EOF _s	0.5	83	0.81	1.4448	51	64
	1.0	150	0.81	0.9011	32	80
	1.5	216	0.85	0.5108	23	86
	2.0	301	0.84	0.3903	16	90

From results presented in Table 2, it can be noted that the values of C_{dl} are directly proportional to the EOF_s concentration, an increase in the concentration of the tested inhibitor leads to a decrease in C_{dl} , which is referred to the adsorption of the EOF_s molecules, resulting in an increase in the film thickness formed on the surface of MS and thus a decrease in the degradation of the metal as well as retardation of hydrogen evolution [43].

2.3. Adsorption isotherm

In order to provide significant information about the adsorption of the chemical compounds used as inhibitors, the adsorption isotherms are very popularly and widely used for the investigation of the interaction types and to provide basic insights about the adsorption modes (chemical, physical, or both) [44, 45]. To find a suitable adsorption isotherm in the present study, several commonly used isotherms were tested, among which the Langmuir adsorption isotherm was found to fit well with our experimental data (Figure 5). The Langmuir isotherm can be represented as [46]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (7)$$

Where C_{inh} is the concentration, K_{ads} is the equilibrium constant of the adsorption process. K_{ads} is related to the standard free energy of adsorption ΔG_{ads}^0 by the following equation [46]:

$$\Delta G_{\text{ads}}^0 = -RT \ln(K_{\text{ads}} \times 999) \quad (8)$$

Where R represents the gas constant and T is the absolute temperature. The value of 999 is the concentration of water in solution in g/L.

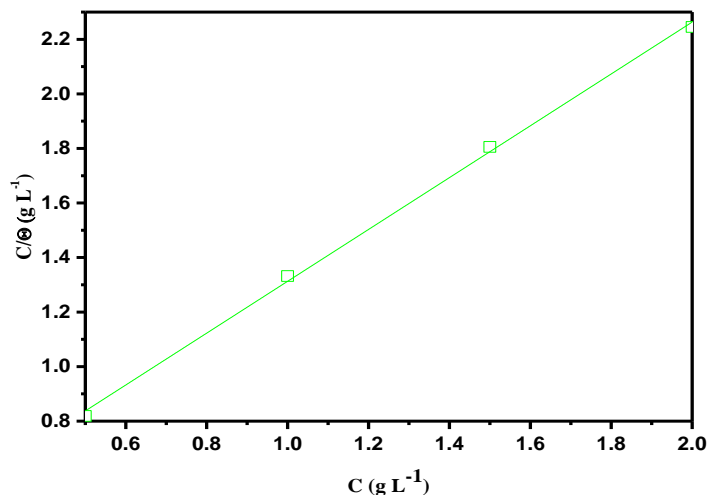


Figure 4. Langmuir adsorption of inhibitor on the mild steel surface in 1 M HCl solution at 303 K.

The slopes of the isotherms show a deviation from the value of unity as would be expected for the ideal Langmuir adsorption isotherm equation. This deviation from unity may be due to the interaction among the adsorbed species on the metal surface. The Langmuir isotherm equation is based on the assumption that adsorbed molecules do not interact with one another, but this is not true in the case of organic molecules having polar atoms or groups from heterocyclic compounds which are adsorbed on the cathodic and anodic sites of the metal surface. In addition to the principal active constituent; the EOF_s contain other heterocyclic compounds as well. Therefore it is recommended not to determine ΔG_{ads}^0 values in such situations [47, 48].

2.3. Weight loss study

2.3.1. Effect of concentration

It's very reported that the inhibitive action is the adsorption of the chemical compounds used as corrosion inhibitors on the surface of the metals is mainly due to the presence of reactive sites such as heteroatoms, π -bonds and aromatic rings. These characteristics are

very presented in our EOF_s, which lets us perform weight loss tests as a baseline method in order to obtain basic information about the efficiency of tested compounds. The effect of the addition of EOFs tested at different concentrations on the corrosion of MS in 1 M HCl solution was studied by weight loss measurements at 303 K after 6 h of immersion period and the obtained data are listed in Table 3.

Table 3. Effect of EOF_s concentration on corrosion data of mild steel in 1 M HCl.

Inhibitor	Concentration (g/L)	C_R (mg cm ⁻² h ⁻¹)	η (%)	θ
Blank	–	1.135	–	–
EOF _s	0.5	0.442	61	0.61
	1.0	0.283	75	0.75
	1.5	0.192	83	0.83
	2.0	0.124	89	0.89

In this section, the weight loss tests further confirm the dependence of the concentration on the efficiency of the tested inhibitor. From the results depicted in Table 3, it is clear that the values of $\eta_w\%$ increased with increasing inhibitor concentration. At 2.0 g/L concentration, EOF_s exhibit the maximum $\eta_w\%$ (89%), while the corrosion rate considerably decreases from 1.135 (in blank test) to 0.124 mg·cm⁻²·h⁻¹ at 2.0 g/L of EOF_s.

2.3.2. Effect of the temperature

The influence of temperature on inhibition efficiency and corrosion rate values was studied by weight loss experiment at different temperatures (303–333 K) in the absence and presence of 2 g/L EOF_s in 1 M HCl. It can be seen in Table 4, as the temperature increases, there is an increase in C_R and a decrease in $\eta\%$ values respectively. This occurs due to the desorption of inhibitor molecules.

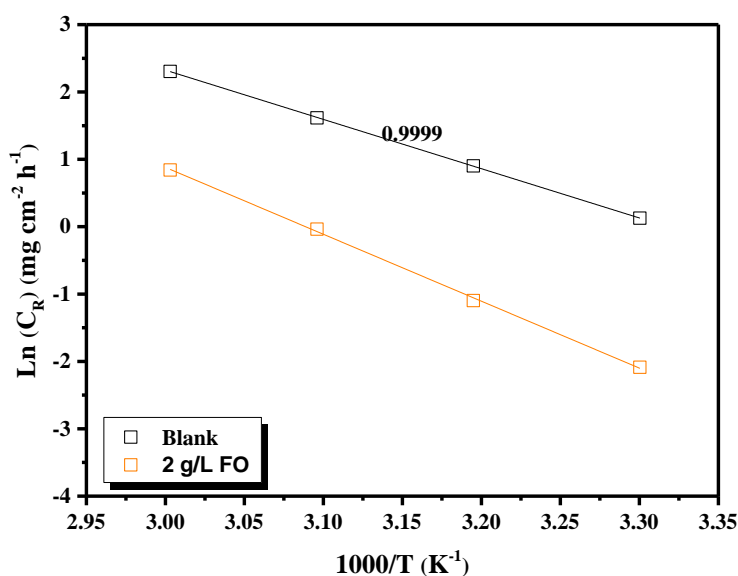
The dependence of corrosion rate on temperature can be expressed by Arrhenius equation[9]:

$$C_R = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

Where E_a represents apparent activation energy, R is the gas constant, A is the pre-exponential factor. The values of E_a were calculated by linear regression between $\ln(C_R)$ and $1/T$ (Figure 5). The value of E_a (Table 6) for an inhibited solution is higher than that for an uninhibited solution. The higher value of E_a in the presence of inhibitor indicates that more energy barrier is required for the corrosion reaction to occur [49].

Table 4. The results of the temperature effect of carbon steel corrosion performed in 1 M HCl and with 2 g/L of EOF_s.

Inhibitor	Temperature (K)	C_R ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	η (%)	θ
Blank	303	1.135	–	–
	313	2.466	–	–
	323	5.032	–	–
	333	10.029	–	–
EOF _s	303	0.124	89	0.89
	313	0.334	86	0.86
	323	0.965	80	0.80
	333	2.318	76	0.76

**Figure 5.** Arrhenius plots of $\ln C_R$ vs. $1/T$ for mild steel in 1 M HCl in the absence and the presence of EOF_s at optimum concentration.

Thermodynamics of mild steel corrosion in 1 M HCl are calculated using an alternative formula of the Arrhenius equation [9]:

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right), \quad (10)$$

Where h is Planck's constant, N is the Avogadro number, R is the universal gas constant, ΔH_a is the enthalpy of activation and ΔS_a is the entropy of activation. Figure 6 shows that

the Arrhenius plots of $\ln(C_R/T)$ versus $1/T$ gave straight lines with slope $(-\Delta H_a/R)$ and intercept $(\ln R/Nh + \Delta S_a/R)$ from where ΔH_a and ΔS_a values were calculated.

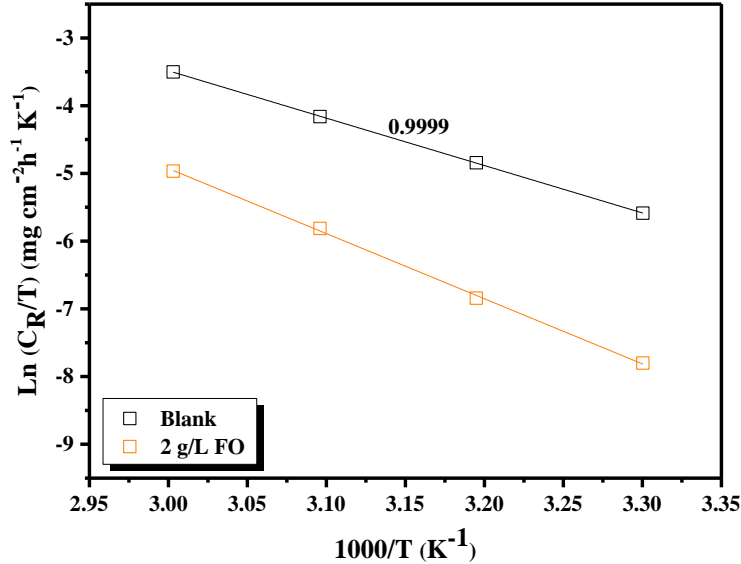


Figure 6. Relation between $\ln(C_R/T)$ and $1000/T$ at different temperatures.

The positive values of ΔH_a in the presence and absence of inhibitor reflect the endothermic nature of steel dissolution. The higher values of ΔS_a might be the result of the adsorption of inhibitor molecules from the 1 M HCl solution, which could be regarded as a quasi-substitution process between these molecules in the aqueous phase and water molecules on the mild steel surface [50].

Table 4. Activation parameters for the mild steel dissolution in 1 M HCL in the absence and the presence of 2 g/L of EOF_s.

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J·mol ⁻¹ ·K ⁻¹)	$E_a - \Delta H_a$
Blank	31.00	28.35	-98.8	2.65
2.0 g/L EOF _s	82.60	79.95	1.4	2.65

Conclusion

The essential oil of fennel seeds (EOF_s) can act as an eco-friendly and biodegradable for the inhibition of the MS corrosion in 1 M of hydrochloric environments. The *PDP* results indicate the mixed type nature of EOF_s, while the *EIS* data show that the C_{dl} decreased when the concentration of EOF_s increases. The same trend of the values of *IE%* of EOF_s is obtained by all used methods. The inhibitory action of EOF_s decreased when the

temperature increases. The adsorption of Fennel essential oil on the steel surface follows the Langmuir isotherm.

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