Plant *Doum* (*Hyphaenethebaica L.*) as a safe corrosion inhibitor for carbon steel in a solution of HCl

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Abstract

Plant *Doum* (*Hyphaenethebaica L.*) extract was studied as a corrosion inhibitor for carbon steel (CS) dipped in 1 M hydrochloric acid using chemical and electrochemical tests. From chemical tests based on mass loss (ML), the inhibition efficiency increased with increasing the concentration of *Doum* (*Hyphaenethebaica L.*) extract (up to 150 ppm). The adsorption isotherm of *Doum* (*Hyphaenethebaica L.*) extract on CS surface obeys the Langmuir adsorption isotherm. The inhibition efficiency improves on raising the concentration of the *Doum* (*Hyphaenethebaica L.*) extract and decreases with an increase in the temperature of the medium. This extract may form a film which acts as a barrier decreasing the contact area between the CS surface and the HCl solution. *Doum* (*Hyphaenethebaica L.*) extract acts as mixed inhibitor in HCl solution without modifying the mechanism of hydrogen evolution. From the EIS examination, we notice that with an increase in the concentration of *Doum* (*Hyphaenethebaica L.*) extract, the double layer capacitance decreased, but the charge transfer resistance increased. Thermodynamic parameters of activation and adsorption were calculated and explained. The sign of the free energy of adsorption implies that the adsorption process is spontaneous. The surface morphology of CS was examined by employing the SEM technique. The results obtained by all the methods are in good harmony.

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Introduction

Corrosion is a naturally occurring phenomenon that has an influence on society by degrading household products, automobiles, airplanes, public roads, bridges, and distribution systems [1]. The main reason of the corrosion of metals is their tendency to reach the stable state. Many metal alloys are in unstable state and interact with the environment to reach the minimum energy by forming metal complexes [2]. Carbon steel is used in many industries such as refinery of oil and gas, bridges, and machines. Hydrochloric acid is used in many fields such as pickling of metals, cleaning of boilers, acidizing of oil wells, and recovery of ion exchangers. In addition, HCl is one of the acids that are widely used in improving the productivity (stimulation) of wells in oil and gas production, and over several years it has

been utilized to increase the primary productivity of new wells and restore the productivity of old wells [3]. Acids enhance the metal dissolution rate and are responsible for material damage. There are several methods to control the process of metal corrosion, but one of the most significant practical methods used is by utilizing corrosion inhibitors in the industrial field as well as in academic studies [4]. Corrosion inhibitors are defined as those substances that, if added in small amounts to corrosion solutions, can lower or prevent the interaction of metals with these environments. Some inhibitors are organic compounds that contain heteroatoms such as nitrogen, oxygen, and sulfur atoms, in addition to the many existing bonds, all of which help them adsorb on the surface of the metal and protect it from corrosion [5]. Naturally occurring corrosion inhibitors are environmentally friendly, available, inexpensive, and are obtained from renewable sources [6–13].

In the present research, we studied the environmentally friendly materials *Doum* (*Hyphaenethebaica* L.) extract as an inhibitor of CS corrosion in 1 M HCl solution. *Hyphaenethebaica* L. was chosen due to its properties: it contains many organic compounds that are ideal for protecting metals, is cheap and available. Several methods were used to study the inhibition behavior, including electrochemical and ML methods, in addition to studying the metal surface by scanning electron microscopy (SEM).

Materials and Methods

The samples were prepared from carbon steel whose composition is shown in Table 1.

Table 1. Chemical analysis of the components (wt. %) of carbon steel.

Element	C	Si	Mn	P	S	Ni	Cr	Mo	V	Cu	Al	Fe
(wt. %)	0.09	0.22	1.52	0.01	0.05	0.04	0.02	0.004	0.002	0.02	0.04	Rest

Solutions

The hydrochloric acid solution (6 M) was prepared from 37% hydrochloric acid using double distilled water and then titrated with 1 M sodium carbonate. Using the prepared HCl, 1.0 M HCl solutions were prepared, without or with various concentrations of *Doum* (*Hyphaenethebaica* L.) extract ranging from 25 to 150 ppm. 1000 mL stock solutions (1000 ppm) of the studied plant extract were prepared by dissolving a suitable mass of the *Doum* (*Hyphaenethebaica* L.) extract (1.0 g) in a certain volume of double distilled water (1.0 L). The tested concentrations which ranged from 25–150 ppm were prepared by dilution of the stock *Doum* (*Hyphaenethebaica* L.) extract with double distilled water.

Chemical structure of *Doum* extract

Doum extract contains a variety of phytochemicals including low and moderate amounts of saponin, tannis, hormones, glycosides, flavonoids, terpinids, and terpinines. Oxygenated composite is 66.7% of the whole composites obtained from the extraction process [14].

Figure 1. The major components obtained from the *Doum* extract.

Preparation of plant extract

Fifty grams of field materials obtained from the plant was suspended in 600 mL of double distilled water for two hours in a hydro distillation apparatus for European Pharmacopoeia. The aqueous extracts were then filtered, and the filtrate obtained was concentrated to dryness under vacuum, resulting in the crude extract, which was then suspended in ultra-pure methanol and kept at 4°C until use.

Mass loss (ML) measurements

The ML test involves a study of the dissolution of C-steel in a fresh solution of 1.0 M hydrochloric acid in the presence and absence of various concentrations of the *Doum* (*Hyphaenethebaica L.*) extract. Seven samples were cut and sanded, then washed with double distilled water, dried, and weighed (W^0). The ML measurements were performed by dipping the sheet in 100 mL of corrosive media with and without various concentrations (25 to 150 ppm) of the extract at various temperatures (25–45°C) for a period of 180 min. The samples were removed from the test solution after 30 min, immersed in water, dried and reweighed (W). The inhibition efficiency (%*IE*) and the degree of CS coverage (θ) due to the adsorption of extract molecules on the CS surface were computed by the equation:

$$\%IE = \theta \cdot 100 = \left(\frac{W^0 - W}{W^0} \right) \cdot 100 \quad (1)$$

where, W and W^0 refer to the ML of the CS per unit area in the presence and absence of the *Doum* (*Hyphaenethebaica L.*) extract studied, correspondingly. The corrosion rate (*CR*) was calculated as:

$$CR = \frac{\Delta W}{At} \quad (2)$$

where, ΔW is the mass loss, A is the sample surface area exposed to the solution expressed in cm^2 , and t is the submersion time in min.

Potentiodynamic polarization (PP) measurements

PP tests were performed in a cell comprising three different electrodes, namely a working, reference, and auxiliary electrodes. The working electrode was made of CS, as explained above. Its surface area was 1 cm^2 . Prior to use, the electrode was treated as in the ML tests. The working electrode was placed in the solution at the open circuit potential for 30 minutes to reach the stable state. Polarization curves were recorded at a constant scan rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$ from 0.35 to -1.3 V (SCE) [15]. Experiments were repeated in triplicate. The %IE provided by *Doum* (*Hyphaenethebaica L.*) extract is due to the adsorption of the extract on the CS surface and was calculated by Eq. 3:

$$\%IE_p = \theta \cdot 100 = \left(\frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \right) \cdot 100 \quad (3)$$

Where i_{corr}^0 and i_{corr} are the uninhibited and inhibited corrosion current densities, correspondingly.

AC impedance spectroscopy (EIS) test

EIS was performed by utilizing AC signals from 100 kHz to 100 mHz with a peak amplitude of 10 mV at OCP. The impedance results were fitted by the appropriate equivalent circuit by means of Gamry Echem program, and using the charge transfer resistance (R_{ct}) as a function determining the protection value due to the adsorption of extract molecules on the CS surface. It was computed by the following equation:

$$\%IE_{\text{EIS}} = \theta \cdot 100 = \left(\frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \right) \cdot 100 \quad (4)$$

Where R_{ct} and R_{ct}^0 are the charge transfer resistances in the system inhibited by the *Doum* (*Hyphaenethebaica L.*) extract and in the inhibitor-free system, respectively.

Electrochemical frequency modulation (EFM) test

EFM applied the signal with a value of 10 mV through two sinus waves from 2 to 5 Hz, and the choice depends on three arguments [16]. This technology is fast and non-destructive. Corrosion current density (i_{corr}), causal factors CF2 and CF3, and Tafel slopes (β_a and β_c) were determined through the higher peaks [17]. %IE was computed by equation (3). The EFM study was performed using a Gamry Potentiostat / Galvanostat / ZRA (PCI4-G750). Gamry includes DC105 DC Corrosion program and EIS300 EIS program, the EFM140 for EFM program, as well as a computer for data collection. Echem Analyst version 5.5 was

used to plot, calculate and synthesize data. All electrochemical studies were performed at 25°C.

SEM measurements

The morphological properties of the CS surface were studied. The tests were performed in 1.0 M of HCl in the absence of a corrosion inhibitor and in the presence of the highest concentration of *Doum* (*Hyphaenethebaica* L.) extract (150 ppm). The specimens were dipped in the corrosive solution for one day, washed with double distilled water, dried and studied using utilizing a JEOL JSM-5500 instrument (Japan) at a magnification of x2000.

Results and Discussion

ML tests

The measurements of CS samples were reported after various times of dipping (30, 60, 90, 120, 150 and 180 min) at various temperatures (25, 35, 45, 55°C). The ML graph at 25°C is shown in Figure 1. Table 2 lists the %IE data at various temperatures. The results illustrate that in the presence of *Doum* (*Hyphaenethebaica* L.) extract, the CR of CS samples in 1.0 M HCl solution decreases. The %IE is observed to raise when the concentration of the *Doum* (*Hyphaenethebaica* L.) extract increases. The curves are nearly linear indicating that all the molecules which are added in the tested concentration range find their free surface site to adsorb on. So, every single added molecule directly occupies its part in the inhibitive action. Consequently the %IE rises with an increase in the *Doum* (*Hyphaenethebaica* L.) extract concentration due to the covered surface area of CS.

Figure 2. ML-time curves for the dissolution of CS in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica* L.) extract at 25°C.

Table 2. The temperature effect on %IE of CS in acid environment with and without various concentrations of *Doum* (*Hyphaenethebaica* L.) extract.

Temp., °C	Concentration, ppm					
	25	50	75	100	125	150
	%IE					
25	76.0	77.8	80.2	82.6	85.4	88.9
35	70.6	73.2	76.7	79.2	82.1	84.9
45	58.6	62.6	66.3	70.7	74.0	77.8
55	46.4	49.5	53.1	58	62.4	67.5

Adsorption isotherm

Studying the adsorption isotherm helps explain the reaction occurring between the CS surface and *Doum* (*Hyphaenethebaica* L.) extract. It is understood that θ increases with raising inhibitor concentration; this is because of the adsorption of *Doum* (*Hyphaenethebaica* L.) molecules on the CS surface. It is also supposed that the adsorption of the studied *Doum* (*Hyphaenethebaica* L.) extract occurs with monolayer adsorption so that the adsorption process may obey the Langmuir isotherm. For the investigation of the adsorption mechanism the following equation was applied:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (6)$$

Where, C refers to the concentration of *Doum* (*Hyphaenethebaica* L.) extract in the electrolyte and K_{ads} represents the equilibrium constant of the adsorption process. Commonly, the CR of CS in an acid environment improves with an increase in temperature. The ΔG_{ads}^0 values at all calculated temperatures can be obtained from the following Eq. [18]:

$$K_{\text{ads}} = (1/55.5) \exp\left(\frac{-\Delta G_{\text{ads}}^0}{RT}\right) \quad (7)$$

Where, 55.5 refers to the concentration of water in (M) at the CS/solution interface. ΔH_{ads}^0 was determined from Eq. (8) which is defined as Van't Hoff:

$$\log K_{\text{ads}} = \frac{-\Delta H_{\text{ads}}^0}{2.303RT} + \text{constant} \quad (8)$$

The heat of adsorption (ΔH_{ads}^0) was computed by drawing $\log K_{\text{ads}}$ versus $1/T$ as shown in Figure 4. The slope of lines equal to $(-\Delta H_{\text{ads}}^0/R)$. Then the following Eq. 9 was applied [19]:

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0 \quad (9)$$

From the values of ΔG_{ads}^0 and ΔH_{ads}^0 in Eq. (9), ΔS_{ads}^0 values were obtained at all investigated temperatures. Table 3 reports the thermodynamic parameters of the studied *Doum* (*Hyphaenethebaica* L.) extract on CS surface in 1.0 M hydrochloric acid medium. ΔG_{ads}^0 data in the Table confirm the spontaneous adsorption of the extract on the CS surface. The negative free energy values decrease with increasing temperature, which confirms that the adsorbed layer is more stable at low temperatures [24]. From our previous knowledge, we know that the free energy results confirm that the type of adsorption is physical adsorption rather than chemical adsorption as it is known that negative values smaller than 20 kJ/mol correspond to physical adsorption, in agreement with the results obtained here. These results demonstrate that the adsorption is mainly physical adsorption [20, 21]. ΔH_{ads}^0 values obtained from measurements with values smaller than 100 kJ·mol⁻¹ indicate that the adsorption type is physisorption. The negative signs of ΔH_{ads}^0 values with addition of the *Doum* (*Hyphaenethebaica* L.) extract explains the exothermic nature. The entropy of adsorption, ΔS_{ads}^0 in the presence the *Doum* (*Hyphaenethebaica* L.) has negative sign and is small in agreement with an exothermic process [22]

Figure 3. Curves of Langmuir adsorption on CS in the absence and presence of various concentrations of *Doum* (*Hyphaenethebaica* L.) extract.

Figure 4. Line of $\log K_{\text{ads}}$ vs. $1000/T$ for the adsorption of *Doum* (*Hyphaenethebaica* L.) extract on CS in 1 M HCl.

Table 3. Parameters of Langmuir adsorption for adsorption of *Doum* (*Hyphaenethebaica* L.) extract on the CS surface at various temperatures.

Temp. K	$-\log K_{\text{ads}}$	$-\Delta G_{\text{ads}}^0$ $\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta H_{\text{ads}}^0$ $\text{kJ}\cdot\text{mol}^{-1}$	$-\Delta S_{\text{ads}}^0$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
298	2.0400	21.6	34.4	72.3
308	1.9674	21.5	34.4	71
318	1.7331	21.2	34.4	66.5
328	1.5022	20.4	34.4	62.1

The effect of temperature on the adsorption process

The impact of temperature on the CS dissolution in 1.0 M HCl environment in the absence and in the presence of various concentrations of the *Doum* (*Hyphaenethebaica* L.) extract was investigated at various temperatures (25, 35, 45, and 55°C) by ML tests and are presented in Table 2. From these results, it is obtained that an increase in temperature results in increase in *CR*, so the %*IE* of the *Doum* (*Hyphaenethebaica* L.) extract decreases. These data are listed in Table 2. For identifying the kind of adsorption of the *Doum* (*Hyphaenethebaica* L.) extract on the surface of CS, *i.e.*, whether it is chemical or physical, ML tests were carried out at four temperatures. It is noted that the effect of temperature on the corrosion of CS pieces used in the investigation and dipped in 1 M of hydrochloric acid was studied in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica* L.) extract. It has been found that on increasing the concentration from 25 ppm to 150 ppm, the degree of protection rises in contrast to the *CR*. The activation energy can be estimated from the Arrhenius equation:

$$k_{\text{corr}} = A \exp\left(\frac{-E_a^*}{RT}\right) \quad (10)$$

Where, E_a^* is the activation of energy of CS in corrosive environment in the presence and absence of *Doum* (*Hyphaenethebaica L.*) extract, and A is the exponential factor of the Arrhenius equation. Plots of $\log k_{\text{corr}}$ versus $(1/T)$ for CS in 1 M hydrochloric acid in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica L.*) extract are presented in Figure 5 showing straight lines. The values of E_a^* calculated from the slopes of straight lines that equal $(-E_a^*/2.303R)$ are documented in Table 4. It obvious that E_a^* increases with a raising concentration of *Doum* (*Hyphaenethebaica L.*) extract, showing that the energy barrier for the corrosion reaction raised and demonstrating that adsorption of *Doum* (*Hyphaenethebaica L.*) extract molecules on CS surface is physical. The ΔS^* , and ΔH^* values were determined from the transition state theory by applying the following equation [23]:

$$k_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (11)$$

Figure 4. Arrhenius plots ($\log k_{\text{corr}}$ vs. $1/T$) for dissolution of CS in 1 M hydrochloric acid without and *Doum* (*Hyphaenethebaica L.*) extract.

A plot of $\log(k_{\text{corr}}/T)$ versus $(1/T)$ also gave straight lines as shown in Figure 6 for CS dissolution in 1 M HCl in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica L.*) extract. The slopes of the lines are used to calculate enthalpy $-\Delta H_a^*/2.303R$, and the activation entropy is calculated using the intercept of the lines $[\log(R/Nh) + \Delta S_a^*/2.303R]$. The values of these parameters (ΔH^* and ΔS^*) are listed in Table 4. The measured ΔH^* reflects an endothermic process. The calculated values of ΔS^*

in the presence and absence of *Doum* (*Hyphaenethebaica L.*) extract are large and negative; this indicates that the activated complex in the rate-determining step prefers an association rather than dissociation step.

Figure 5. $\log k_{\text{corr}}/T$ vs. $(1/T)$ for dissolution of CS in 1 M hydrochloric acid without and with of *Doum* (*Hyphaenethebaica L.*) extract.

Table 4. E_a^* , ΔH^* and ΔS^* data for dissolution of CS in 1 M hydrochloric acid without and with various concentrations of *Doum* (*Hyphaenethebaica L.*) extract.

C_{inh} (ppm)	E_a^* $\text{kJ} \cdot \text{mol}^{-1}$	ΔH^* $\text{kJ} \cdot \text{mol}^{-1}$	$-\Delta S^*$ $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
0	37.6	15.72	145.5
25	59.9	25.42	84.12
50	60.3	25.59	83.56
75	61.5	26.08	80.82
100	61.8	26.22	80.79
125	63.5	26.97	76.48
150	66.7	28.38	67.61

PP tests

The PP diagrams of CS in 1.0 M HCl in the presence of and absence of various concentrations of the *Doum* (*Hyphaenethebaica L.*) extract at 25°C are shown in Figure 6. From Figure 6, we see that both cathodic (hydrogen discharge) and anodic (CS dissolution) reactions are inhibited upon adding various concentrations of *Doum* (*Hyphaenethebaica L.*) extract. The electrochemical parameters E_{corr} , θ , %IE, and i_{corr} were measured and are given

in Table 5. The data show that on addition of *Doum* (*Hyphaenethebaica* L.) extract, the values of i_{corr} decrease while the values of E_{corr} do not change significantly [24, 25]. So, the *Doum* (*Hyphaenethebaica* L.) extract performs as a mixed kind inhibitor. The parallel Tafel lines indicate that there is no mechanism change with and without the extract.

Figure 6. The PP curves of CS dissolution in 1.0 M hydrochloric acid in the presence of and in the absence of various concentrations of *Doum* (*Hyphaenethebaica* L.) extract at 25°C.

Table 5. Electrochemical parameters i_{corr} , E_{corr} , k_{corr} , θ and %IE of CS in 1 M HCl with various concentrations of *Doum* (*Hyphaenethebaica* L.) extract.

C_{inh} , ppm	i_{corr} , $\mu\text{A}\cdot\text{cm}^{-2}$	$-E_{\text{corr}}$, mV vs. SCE	CR $\text{mm}\cdot\text{y}^{-1}$	θ	%IE
Blank	734	428	335.5	—	—
25	291	462	133.1	0.60	60.4
50	218	475	99.6	0.70	70.3
75	201	479	91.8	0.73	72.6
100	183	502	83.78	0.75	75.1
125	177	438	80.66	0.76	75.9
150	150	504	68.4	0.80	79.6

AC impedance spectra (EIS)

Nyquist plots recorded on the CS at potentials established after 30 min dipping in 1.0 M hydrochloric acid in the presence and absence of various concentration of *Doum* (*Hyphaenethebaica* L.) extract. The attained Nyquist and Bode plots for *Doum* (*Hyphaenethebaica* L.) extract are displayed in Figures 8, 9. The Nyquist plot has the shape of a semicircle loop. This indicates that the charge transfer process refers to the dissolution

of CS metal [22]. The equivalent circuit defined for CS and electrolyte is shown in Figure 10. The impedance values and %IE for CS in 1 M hydrochloric acid in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica L.*) extract are depicted in Table 6. Figures 8 and 9 show the low frequency region, and in the presence of *Doum* (*Hyphaenethebaica L.*) extract, the impedance values rise compared to the absence of the *Doum* (*Hyphaenethebaica L.*) extract, the radius of the circle rises when the concentration of the *Doum* (*Hyphaenethebaica L.*) extract increases and hence, the charge transfer resistance in corrosion reactions increases. From all the above, there is high resistance established as the result of adsorption of the *Doum* (*Hyphaenethebaica L.*) extract at the CS/solution interface [26]. The double layer capacitance C_{dl} may be calculated using the CPE parameters (Y_0 and n), which are described in the following Eq. 12:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (12)$$

Where Y_0 is the magnitude of the CPE and n is the variance of the CPE data: $-1 < n < 1$. Table 6 shows that when the concentration of *Doum* (*Hyphaenethebaica L.*) extract is increased, the values of C_{dl} decrease, which may be explained by a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer [27]. This is due to the adsorption of *Doum* (*Hyphaenethebaica L.*) molecules on the CS/solution interface and formation of a protective film on this interface. Table 6 lists the values of parameters such as R_s and R_{ct} obtained by EIS fitting as well as the derived parameters C_{dl} and %IE.

Figure 8. Nyquist plots for CS dissolution in the presence and absence of *Doum* (*Hyphaenethebaica L.*) extract.

Figure 9. Bode plots for CS dissolution in *Doum* (*Hyphaenethebaica L.*) extract in the presence and absence of extract.

Figure 10. Electric circuit used to match the EIS results.

Table 6. The results of electrochemical impedance experiments for the dissolution of CS in 1.0 M hydrochloric acid at various *Doum* (*Hyphaenethebaica L.*) extract concentrations.

C_{inh} (ppm)	Y_0 , $(\mu\Omega^{-1} \cdot s^n \cdot cm^{-2}) \cdot 10^{-6}$	n	R_{ct} , $Ohm \cdot cm^2$	C_{dl} , $\mu F \cdot cm^{-2}$	%IE
0	398	0.854	8.95	152	—
25	142	0.821	24.62	41	63.6
50	112	0.837	27.92	36	67.9
75	88	0.851	32.62	31	72.5
100	72	0.848	42.96	25	79.1
125	64	0.857	43.08	23	79.2
150	52	0.863	48.35	20	81.5

EFM tests

The electrochemical corrosion kinetic measurements at various concentrations of the *Doum* (*Hyphaenethebaica L.*) extract in 1.0 M hydrochloric acid at 25°C are presented in Table 7. The %IE values were computed from Eq. (3) and it is observed that with an increase in the concentration of the *Doum* (*Hyphaenethebaica L.*) extract, %IE increased. The causality factors CF2 and CF3 listed in Table 7 indicate that the results obtained are of good quality. By analysis of the results obtained from Figure 11 and Table 7 it is concluded that, upon raising the concentration of the *Doum* (*Hyphaenethebaica L.*) extract, the values of corrosion current densities are reduced and an increase in the %IE occur. The acquired CF2 and CF3 values are close to the theoretical ones (2, 3), resulting in satisfactory findings [28].

Figure 11. EFM spectra of CS in the presence and absence of various concentrations of *Doum* (*Hyphaenethebaica L.*) extract at 25°C.

Table 7. Electrochemical kinetic parameters from EFM test for dissolution of CS in 1 M hydrochloric acid solutions in the presence and absence of various concentrations of the *Doum* (*Hyphaenethebaica* L.) extract.

C_{inh} , ppm	i_{corr} , $\mu A \cdot cm^{-2}$	CF2	CF3	θ	%IE
0	884	1.9	3.3	—	—
25	518.2	1.9	3.2	0.41	41.4
50	451.5	2.1	3	0.49	48.9
75	344.7	1.8	3.1	0.61	61
100	283.9	1.9	2.8	0.68	67.9
125	225.7	1.8	3.6	0.74	74.5
150	186.4	1.8	3.8	0.79	78.9

Scanning electron microscopy (SEM) investigation

Figure 12. SEM of pure CS surface (a), after immersion in 1 M HCl for 8 hours (b) and after dipping in the corrosive media containing 150 ppm *Doum* (*Hyphaenethebaica* L.) extract for 8 hours (c).

The micrographs of CS specimens in the presence and absence of 150 ppm *Doum* (*Hyphaenethebaica* L.) extract after 8 hours of dipping in 1.0 M hydrochloric acid are shown in Figure 12(a, b, and c). Figure 12(a) refers to the surface of pure CS. Figure 12(b) represents the CS upon dipping for 8 hours in a solution of 1 M hydrochloric acid without addition of the plant extract. Figure 12(c) shows the surface of CS upon dipping for 8 hours in a solution of 1.0 M hydrochloric acid with addition of 150 ppm of the plant extract. Figures 12(a, b and c) show that a porous layer or a film of corrosion products cover all the specimen surface. This is an oxide film; the surface was strongly affected, and cracks were noted. The effect of adding the *Doum* (*Hyphaenethebaica* L.) extract on the CS surface demonstrated in

Figure 12(c) indicates that there are no cracks and the surfaces of the specimens are smoother than those without using the extract. This is because of the arrangement of the *Doum* (*Hyphaenethebaica* L.) molecules on the surface of the CS with attachment on the active sites on the CS surface, thus creating a protection of the CS from the corrosive medium by the extract.

Mechanism of inhibition

The phytochemical *Doum* (*Hyphaenethebaica* L.) extract contains flavonoids, terpenes, phenolic acids which are its major chemical constituents [29]. Most of these phytochemicals are organic compounds containing oxygen (O) and nitrogen (N) as polar functional groups. Such a structure favors the formation of a complex with dissolved iron ions. The result indicate the formation of insoluble complexes. These complexes are adsorbed onto the CS by weak forces to form a protecting cover on the CS from the corrosive environment and hence retards the dissolution process. The surface of the CS sample is positively charged in aqueous acid solution [30]. The Cl^- ions get adsorbed on CS surface and turn it to a negatively charged surface, the protonated extract molecules (cationic) get adsorbed on the negatively charged metal surface due to electrostatic attraction. The protonated molecules could adsorb on specimen CS surface as shown in Figure 13.

Figure 13. Extract in 1 M HCl solution is absorbed and inhibits the corrosion of CS.

Conclusions

The investigated *Doum* (*Hyphaenethebaica* L.) extract in 1.0 M HCl solution is an effective corrosion inhibitor for CS. This plant extract has an inhibition efficacy of 88.9%. The %IE value increases with an increase in the *Doum* (*Hyphaenethebaica* L.) extract concentration and decreases with an increase in the temperature. This suggests that *Doum* (*Hyphaenethebaica* L.) extract being studies is physically adsorbed. The adsorption of *Doum* (*Hyphaenethebaica* L.) extract was found to obey isothermal Langmuir adsorption. The adsorption negative free energy ($-\Delta G_{\text{ads}}^0$) suggests fast and spontaneous adsorption of the

extract on the surface of CS. The adsorbed protective film on the surface of CS ensures that the plant extract has high inhibitive effect. This study demonstrates that this extract is a significant, ecologically friendly, and low-cost inhibitor.

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