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LINSEED OIL AS A NOVEL ECO-FRIENDLY CORROSION INHIBITOR OF CARBON STEEL IN 1 M HCl

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The extraction of linseed oil (LO) was realized by refluxing method. The extracted oil was identified by gas chromatography method coupled with mass spectrometry (GC-MS). In order to contribute to the protection of the environment, one contemplates to try on LO as a green corrosion inhibitor. The corrosion inhibition of LO was studied by weight loss and electrochemical methods. The obtained results showed that the LO is an effective inhibitor of the carbon steel corrosion in 1 M HCl solution, the inhibition efficiency increased with concentration to reach 88% at 200 ppm. Furthermore, the adsorption of the inhibitor on the surface of metal in 1 M HCl solution was found to obey Langmuir's adsorption isotherm. The influences of temperature were also studied in the range from 298 K to 328 K. The kinetic and thermodynamic data of activation dissolution process were determined and discussed.

Keywords: Linseed oil; GC-MS; weight loss; electrochemical method; carbon steel.

1. Introduction

The metallic corrosion affects most industries and can cost billions of dollars each year.¹ In industrial processes, the hydrochloric acid is mostly used for stripping agents, industrial cleaning, descaling as well as in petrochemical processes, etc.^{2,3} It causes the degradation of the metals, either by chemical or electrochemical reactions. There are several methods available to protect metals against corrosion such as the use of a protective barrier by cathodic electrodeposition, the

use of anti-rust solutions or the addition of corrosion inhibitors.

Currently, research in corrosion is focused on "green corrosion inhibitors", that show good inhibition efficiency with low risk of environmental pollution.⁴ The term "green inhibitor" or "ecofriendly inhibitor" refers to substances that are biocompatible such as plant extracts since they are of biological origin.⁵ Thus natural products (derived from plant materials are being studied for their corrosion inhibition potential as

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they are showing good corrosion protection and are more environmentally friendly.^{6,7}

The synthetic compounds acting as the good anti-corrosion are often highly toxic to the environment.⁸ However the green corrosion inhibitors such as oils and plant extracts can be used to replace them in order to protect the metal against the corrosion in an acidic environment.⁹

Linseeds are cultivated in more than 50 countries around the world to produce oil and fiber.¹⁰ They contain about 36% to 40% of oil which is generally used for the manufacture of paints, varnishes, inks, soap, etc.^{11,12} and beneficial foods for health.^{13,14} Fatty acids obtained by extraction of linseed oil (LO) in the Agadir region were used as inhibitors of carbon steel corrosion in 1 M HCl medium.¹⁵

The aim of this work is to use raw LO extracted from linseeds from the region of Kenitra in Morocco. The analysis of this LO by gas chromatography method coupled with mass spectrometry (GC-MS) shows a difference in the chemical compositions by comparison with the oils of linseeds of the other regions. This LO was investigated as green inhibitor of the carbon steel corrosion in 1 M HCl solution. It was studied by gravimetric (weight loss), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). From this experimental study, the thermodynamic parameters such as activation energy, entropy of adsorption and activation enthalpy were determined.

2. Materials and Methods

2.1. Extraction and characterization

The harvesting of flax seed was made at the end of July 2014 at Dar El Gueddari region in Kenitra, Morocco.

2.1.1. Extraction of LO

In a 250-ml flask, 50 g of flax seed is placed in 150 ml of hexane and the mixture is heated at reflux for 4 h.

The solution obtained is filtered and the obtained filtrate is evaporated under vacuum at 313 K. The obtained oil is golden yellow with a yield of 30%.

2.1.2. Characterization and chemical composition of LO

The GC-MS measurements are carried out at the National Centre for Scientific and Technical Research (CNRST) using "Trace GC Ultra/Polaris Q MS" equipment. The collected results (Table 2) show the presence of 12 main components of the extracted oil.

2.2. Experimental study of the carbon steel corrosion inhibition using LO as green inhibitor

2.2.1. Materials

The chemical composition (%) of the carbon steel used in this work is given in Table 1.

2.2.2. Solution

LO is used as inhibitor in a solution of 1 M HCl prepared by dilution of the commercial hydrochloric acid solution (37%) with distilled water. The concentration of LO employed varies from 50 ppm to 300 ppm.

2.2.3. Weight loss measurements

Gravimetric measurements were carried out using 50 ml of the electrolyte in a 100-ml beaker. The sample carbon steel is in rectangular form with initial dimensions of $0.3 \times 2.5 \times 1$ cm. The immersion time for weight loss was 4 h at $25^\circ\text{C} \pm 2^\circ\text{C}$. The experimentation was carried out under stationary state and the solutions are aerated. The experiments were performed as per ASTM practice standard G-31. Duplicate experiments are performed in each case, and the mean value of the weight loss is reported. Before each measurement, polishing was done with abrasive paper of grain size 60–1200, followed by

Table 1. Chemical composition (in wt.%) of carbon steel.

Elements	C	Si	Mn	Cr	Mo	Ni	Al	Cu	Co	V	W	Fe
wt.%	0.11	0.24	0.47	0.12	0.02	0.1	0.03	0.14	<0.0012	<0.003	0.06	Balance

washing with distilled water, degreasing with acetone and drying.

2.2.4. Electrochemical measurements

The electrochemical experiments were performed in a Pyrex cell, equipped with three electrodes: steel electrode about 1 cm^2 of dimension as a working electrode, platinum as an auxiliary electrode and Ag/AgCl as a reference electrode.

The current–potential curves were obtained by the potentiodynamic mode. The scan rate was 1 mV/s started from an initial potential of -900 mV/SCE to -100 mV/SCE . We chose a relatively low scan rate in order to have a quasi-stationary regime. Before recording each curve, a stabilization time of 30 min was allowed to attain a stable value for open circuit potential. The measurements are performed with a composition including a potentiostat–galvanostat PGZ100 radiometer type, associated with software VoltaMaster 4.

The EIS measurements were carried out using a transfer function analyzer (VoltaLab PGZ 100), with a small amplitude AC signal (10 mV rms), over a frequency domain from 100 kHz to 100 mHz with five points per decade. The EIS diagrams were done in the Nyquist representation. The results were then analyzed in terms of an equivalent electrical circuit using Bouckamp program. In order to ensure reproducibility, all experiments were repeated three times. The evaluated inaccuracy did not exceed 10%.

3. Results and Discussion

3.1. Composition of LO

The essential oils were analyzed by GC-MS using the Thermo Fisher apparatus. The spectra are given in Fig. 1 and the main results are summarized in Table 2.

Regarding the chromatographic analysis of LO by GC/MS, we found that 12 compounds represent 95.6% of LO with Tricyclo[4.1.0.0 (2,7)hept-3-ene (75.94%), 4-methyl-2-pentanol (7.76%), oleic acid (4.12%) and 1,4-dimethyl benzene (2.56%) being the major constituents (Table 2). These compounds were thought to be good candidates for corrosion inhibition due to the presence of heteroatoms (O), polar functional groups $-(\text{OH})$, electron donating $-(\text{CH}_3)$

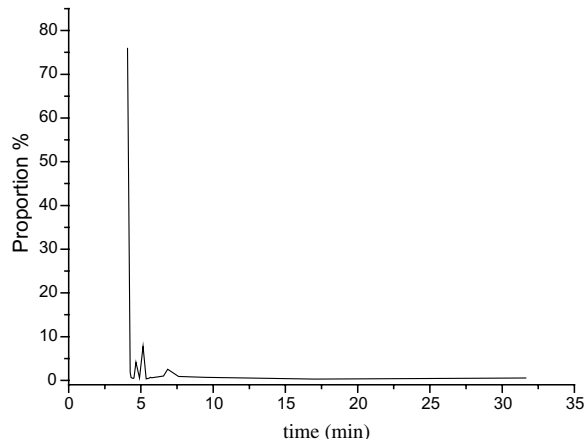


Fig. 1. Chromatogram of LO.

group, π -electrons and aromatic rings as adsorption centers.

3.2. Experimental study of LO as corrosion inhibitor of carbon steel

3.2.1. Gravimetric measurements

The corrosion rate of carbon steel is determined gravimetrically after an immersion time of 4 h at 298 K in 1 M HCl in the absence and in presence of LO at different concentrations. The inhibitory efficiency (EI%) of this oil is calculated through the following equation:

$$\text{EI}\% = \frac{w - w'}{w} \times 100, \quad (1)$$

where w and w' are the corrosion weight losses of carbon steel in the absence and in presence of inhibitor. The mean value of the corrosion weight losses ($\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$) was determined and calculated using the following equation:

$$\omega_{\text{corr}} = \frac{m_i - m_f}{S \times t}, \quad (2)$$

where m_i , m_f , S and t denote initial weight, final weight, surface of specimen and immersion time, respectively.

Corrosion parameters, namely W and inhibition efficiency (EI%) of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of inhibitor obtained from weight loss measurements are shown in Table 3. It appears that the inhibition efficiency increased by increasing the concentration of the inhibitors. This increase is more notable at the optimal concentration of 200 ppm and the value

Table 2. The obtained results by the chromatogram interpretation of the studied LO.


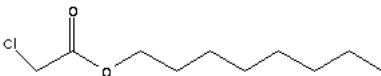
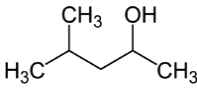
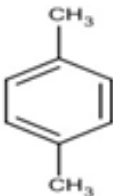
Compounds	Retention time	Proportion (%)	Molecular weight (g/mol)	Compound structure	Molecular formula
Tricyclo[4.1.0.0(2,7)]hept-3-ene	4.07	75.94	92.138		C ₇ H ₈
Oleic acid	4.32	0.63	281.453	—	—
(2'-Nitro-2'-propenyl)cyclohexane	4.45	0.47	169.221	—	—
Chloroacetic acid, octyl ester	4.65	4.12	206.709		C ₁₀ H ₁₉ ClO ₂
1,4-diphenylbut-3-ene-2-ol	4.90	0.55	224.298	—	—
4-methyl-2-pentanol	5.14	7.76	130.228		C ₆ H ₁₄ O
Methoxyacetic acid, cyclohexyl ester	5.66	0.68	172.222	—	—
7-methyl-tetracyclo[4.1.0.0(2,4).0(3,5)]heptane	6.56	1.00	106.165	—	—
1,4-dimethyl benzene	6.85	2.56	106.165		C ₈ H ₁₀
12,15-Octadecadienoic acid	7.61	0.88	280.445	—	—
1,2-Dihydro-1,4-diphenylphthalazine	9.44	0.69	284.355	—	—
2-(5-chloro-2-methoxyphenyl)pyrrole	17.05	0.32	207.656	—	—

Table 3. Corrosion rate and the inhibitory effectiveness of the corrosion in 1 M HCl in the absence and in presence of LO at 298 K.

Inhibitor	Concentration (ppm)	W (mg · cm ⁻² · h ⁻¹)	EI (%)
Blank	00	0.25	—
LO	50	0.051	80
	100	0.048	81
	200	0.030	88
	300	0.063	75

reaches a maximum 88%. By increasing the inhibitor concentration, the part of metal surface covered by inhibitor molecules increases, and that leads to an increase in the inhibition efficiencies.¹⁶

3.2.2. Electrochemical study

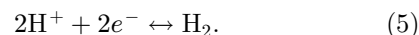
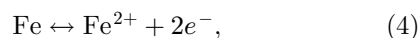
3.2.2.1. Polarization curves

The inhibition efficiency (EI%) is defined as follows:

$$EI\% = \frac{i_{\text{corr}} - i_{\text{corr}/\text{inh}}}{i_{\text{corr}}} \times 100, \quad (3)$$

where i_{corr} and $i_{\text{corr}/\text{inh}}$ are, respectively, the current densities of the corrosion in absence and in presence of the inhibitor. They are obtained by the extrapolation of the cathodic and anodic Tafel rights in the corrosion potential (E_{corr}).

Figure 2 shows the polarization curves of carbon steel in 1 M HCl in absence and in presence of LO at various concentrations ranging from 50 ppm to 300 ppm at 298 K. It is known that the electrochemical reactions of the carbon steel in acidic medium, in the absence of inhibitors, is the anodic dissolution reaction of iron and cathodic reactions related to the proton reduction:



However, in the presence of inhibitor, a shift of the corrosion potential E_{corr} toward more negative values for LO was observed. So, a great definite change on the corrosion potential (E_{corr}) was observed. According to Riggs,^{17,18} if the displacement in E (i) is >85 mV/ E_{corr} , the inhibitor can be seen as a cathodic

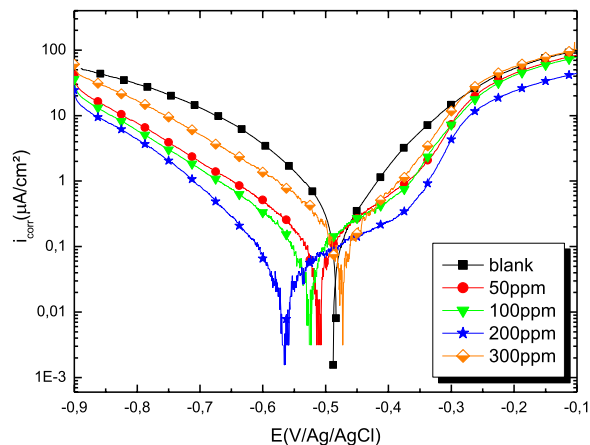


Fig. 2. (Color online) Polarization curves of carbon steel in 1 M HCl at different concentrations of LO at 298 K.

or anodic type, and (ii) if displacement in E is $<85 \text{ mV}/E_{\text{corr}}$, the inhibitor can be seen as mixed type. In our study, the displacement in the case of LO was less than $85 \text{ mV}/E_{\text{corr}}$, which indicated that LO were the mixed type inhibitor.

In addition, it is clear that the current density decreases with increasing of the LO concentration; this indicates that these inhibitors are adsorbed on the metal surface and hence inhibition occurs. The potentiodynamic polarization curves (Fig. 2) show that these inhibitor have an effect on both, the cathodic and anodic slopes (β_c and β_a) and suppressed both cathodic and anodic processes. This indicated a modification of the mechanism of cathodic hydrogen evolution (Eq. (5)) as well as anodic dissolution of iron (Eq. (4)), which suggest that LO powerfully inhibit the corrosion process of carbon steel, and their ability as corrosion inhibitor is enhanced as their concentrations are increased. The suppression of cathodic process can be due to the covering of the carbon steel surface with monolayer due to the adsorbed inhibitor molecules.

Figure 2 shows the cathodic and anodic polarization curves of the carbon steel in 1 M HCl in absence

and in presence of LO at different concentrations. Polarization curves analysis shows that the addition of the oil causes a displacement of the potential corrosion toward more cathodic values. This displacement is accompanied by a net decrease of the cathodic current densities.

The potentiodynamic polarization parameters deduced from these curves are shown in Table 4. One notices a decrease of the cathodic current density with increasing concentration of inhibitor. This density reaches a minimum value of $55 \mu\text{A}/\text{cm}^2$ at a 200 ppm of inhibitor (LO), this indicates the inhibition of the hydrogen release reaction. It can be concluded that it is a cathodic inhibitor, and the curves of the parallel cathodic Tafel show that the hydrogen evolution is controlled by the pure mechanism of activation.^{19,20}

The treatment of these parameters shows that the addition of the inhibitor leads to the corrosion current as long as the concentration in LO increases till density decreases gradually to an optimal concentration of 200 ppm. On the contrary, the efficiency increases with the increase of the concentrations of this oil and reaches an 88% at 200 ppm. By comparison with the Tafel slope of the curve obtained in the case of acid alone, a significant decrease is observed in the values of the Tafel slope (β_c) in the presence of LO, this decrease reaches a minimum value at 200 ppm. This result may be explained by forming a film as a layer overlying the metal surface.

3.2.2.2. Electrochemical impedance spectroscopy

Figure 3 presents the Nyquist plots of carbon steel in 1 M HCl, without and with different concentrations of LO at the corrosion potential. It is noted that the Nyquist plot of carbon steel in the absence and presence of all concentrations of inhibitors contains a

Table 4. Electrochemical parameters of the carbon steel 1 M HCl at different concentrations of LO at 298 K.

Inhibitor	Concentration (ppm)	$-E_{\text{corr}}$ (mV/Ag/AgCl)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$-\beta_c$ (mV dec ⁻¹)	EI (%)	Θ
Blank	—	498	467	220	—	—
LO	50	511	78	109	83	0.83
	100	526	73	104	84	0.84
	200	566	55	83	88	0.88
	300	474	104	108	77	0.77

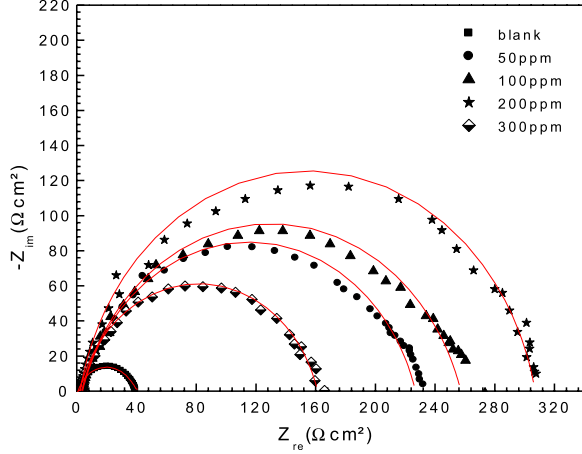


Fig. 3. Electrochemical impedance diagrams of the carbon steel in 1 M HCl in the absence and presence of LO at different concentrations at 298 K.

slightly depressed semi-circular shape, and constant appeared only one time, indicating that carbon steel corrosion is mainly controlled by a charge transfer process. However, it allowed employing constant phase element (CPE) element in order to investigate the inhibitive film properties on metallic surface. Thus, the impedance of the CPE can be described by the following equation:

$$Z_{\text{CPE}} = [Q(j\omega)^n]^{-1}, \quad (6)$$

where j is the imaginary number, Q is the frequency independent real constant, $\omega = 2\pi f$ is the angular frequency (rad s^{-1}), f is the frequency of the applied

signal and n is the CPE exponent for whole number of $n = 1, 0, -1$, CPE is reduced to the classical lump element-capacitor (C), resistance (R) and inductance (L).²¹ The use of these parameters, similar to the CPE, allowed the depressed feature of Nyquist plot to be reproduced readily.

In addition, the effective calculated double layer capacitance (C) is derived from the CPE parameters according to the following equation²²:

$$C = Q^{\frac{1}{n}} \times R^{\frac{(1-n)}{n}}. \quad (7)$$

The Nyquist plots for LO at different concentration in 1 M HCl are presented in Fig. 3. The measured and simulated data fit well enough. According to the above-mentioned equivalent circuits presented in Fig. 5, the solution resistance R_s , the charge transfer resistance R_{ct} and the CPE were fitted and their parameters calculated according to this model are listed in Table 5.

The efficiency of inhibition is measured through the transfer resistor ($E_{R_{\text{ct}}}$ %) which is found by using the following equation:

$$E_{R_{\text{ct}}} \% = \frac{R_{\text{ct}/\text{inh}} - R_{\text{ct}}}{R_{\text{ct}/\text{inh}}} \times 100, \quad (8)$$

where $R_{\text{ct}/\text{inh}}$ and R_{ct} are, respectively, transfer resistances of the charge in the presence and absence of the inhibitor.

As an example, the Bode plots for LO at 200 ppm in 1 M HCl and the inhibited solution were presented in Fig. 4. Figure 4 shows only one depressed capacitive

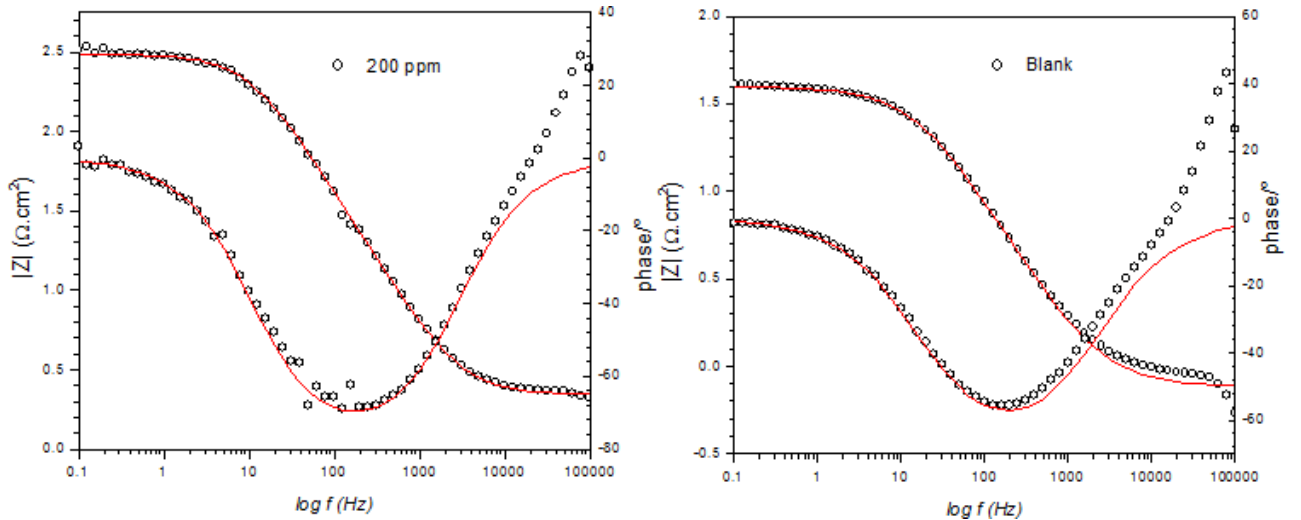


Fig. 4. Bode diagrams for carbon steel in 1 M HCl with and without 200 ppm of LO.

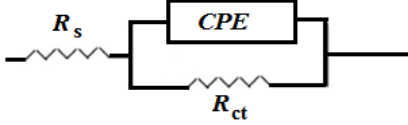


Fig. 5. Electrical equivalent circuit applied for impedance analysis.

loop at the higher frequency (HF) range with one capacitive time constant in the Bode-phase plot.

From Table 5, it may be remarked that R_{ct} values increased, while C_{dl} values decreased with LO concentrations, indicating that more inhibitor molecules are adsorbed onto the metallic surface, providing better surface coverage and/or enhancing the thickness of the protective layer at the metal/solution interface.²³ In addition, these changes in R_{ct} and C_{dl} can be attributed to the gradual displacement of water molecules and/or chloride ions on the carbon steel surface.²⁴ In its turn, the decrease of C_{dl} with concentrations can be explained by the decrease in local dielectric constant and/or the increase in the protective layer thickness on the electrode surface. This trend is in accordance with Helmholtz model, given by the following equation²⁵:

$$C_{dl} = \frac{\varepsilon_0 \times \varepsilon}{e} \times S,$$

where ε is the dielectric constant of the protective layer, ε_0 is the permittivity of free space ($8.854 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$) and S is the effective surface area of the electrode. The inhibitory effectiveness increases with the concentration of the inhibitor to reach a maximum value of 87% at 200 ppm. The values of inhibitory efficiencies of LO determined by the gravimetric method and by stationary and transient electrochemical measurements are in good agreement.

3.2.3. Adsorption isotherms

Adsorption isotherms are very important in understanding the mechanism of organo-electrochemical

reactions.²⁶ In order to evaluate the adsorption process of LO onto carbon steel surface, Langmuir adsorption isotherm was obtained according to the following equations:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \text{ (Langmuir)}, \quad (9)$$

where θ is the surface coverage of the metal surface, K the adsorption-desorption equilibrium constant, C_{inh} the inhibitor concentration and ads is the lateral interaction term describing the molecular interactions in the adsorption layer and the surface heterogeneity. The fractional coverage values θ as a function of inhibitor concentration can be obtained from polarization (LP) and EIS as follows:

$$\theta = \frac{i_{corr} - i_{corr/inh}}{i_{corr}}, \quad (10)$$

$$\theta = \frac{R_{t/inh} - R_t}{R_{t/inh}}. \quad (11)$$

The data were tested graphically, see Fig. 6 by fitting to Langmuir isotherm which is given by Eq. (9).

The analysis of Fig. 6 shows that the variation of the ratio C_{inh}/θ as a function of the inhibitor concentration is linear for the Langmuir isotherm, indicating that the adsorption of the extracts on the surface of the steel in 1 M HCl obeys the Langmuir adsorption isotherm. Consequently, the inhibition of the corrosion is due to the formation of layer on the metallic surface, limiting electrolyte access, the strong correlations ($R^2 = 0.995$) confirm the validity of this chosen model. On the basis of characterization of LO, we postulate that the major constituents act together by adsorption to ensure inhibition. Then, the inhibition is regarded as intermolecular synergistic effect of the various components of essential oil. It is adequately recommended not to determine ΔG_{ads} values since the mechanism of adsorption remains unknown.²⁷

Table 5. Electrochemical impedance parameters in the absence and presence of LO at different concentrations.

Inhibitor	Concentration (ppm)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	n_{ct}	R_{ct} ($\Omega \cdot \text{cm}^2$)	$E\%$	θ
Blank	—	440	0.79	40	—	—
LO	50	44 ± 3	0.82 ± 0.05	240 ± 0.5	83	0.83
	100	35 ± 2	0.82 ± 0.05	270 ± 0.5	85	0.85
	200	50.4 ± 1.7	0.87 ± 0.05	315 ± 0.4	87	0.87
	300	74 ± 6	0.83 ± 0.05	160 ± 0.6	75	0.75

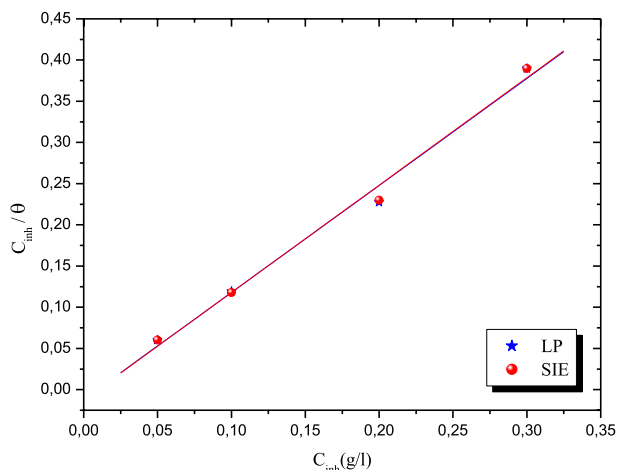


Fig. 6. (Color online) Langmuir adsorption plots obtained from EIS and LP for carbon steel in 1 M HCl containing different concentrations of LO.

3.2.4. Effect of temperature

Temperature is one of the factors that are likely to modify both the behavior of the steel and the nature of the interaction metal/inhibitor in a corrosive environment. The increase in temperature can have a significant impact on the formation of the inhibitory film. Indeed, an increase in temperature would favor the desorption of the inhibitor and a rapid dissolution of the organic compounds or the formed complexes, thus causing a loss of the corrosion resistance of the steel.²⁸

To examine the influence of this parameter on the inhibitory efficacy of oil for the optimal concentration of 200 ppm, we performed measurements of stationary electrochemical potentiodynamic mode in a range of temperatures ranging from 298 K to 328 K. We traced the steel polarization curves with and without LO (Figs. 7 and 8).

To study the effect of temperature on the inhibitory efficiency of LO, the parameters are determined from the potentiostatic polarization curves. The measures are made in absence and presence of an inhibitor in 200 ppm in the range of temperature 298–328 K. The parameters presented in Table 6 suggest that LO adsorbs well on the surface of the steel, in the 1 M HCl solution, in all the studied temperatures and show that the current density of corrosion increases with the increase of the temperature. The increase of the temperature usually accelerates the reactions of corrosion which translates dissolution of the metal

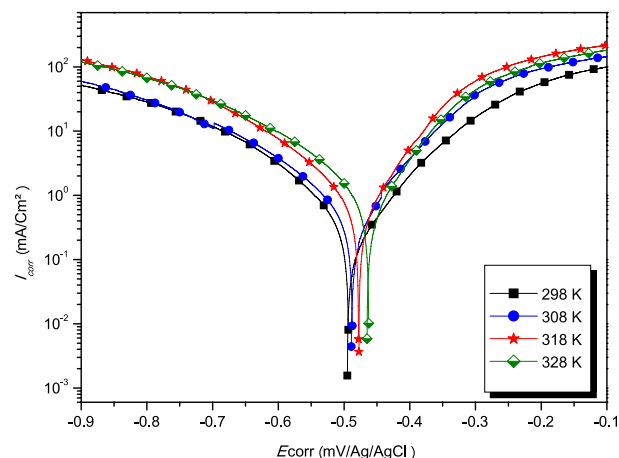


Fig. 7. (Color online) Potentiodynamic polarization curves of carbon steel in 1 M HCl at different temperatures.

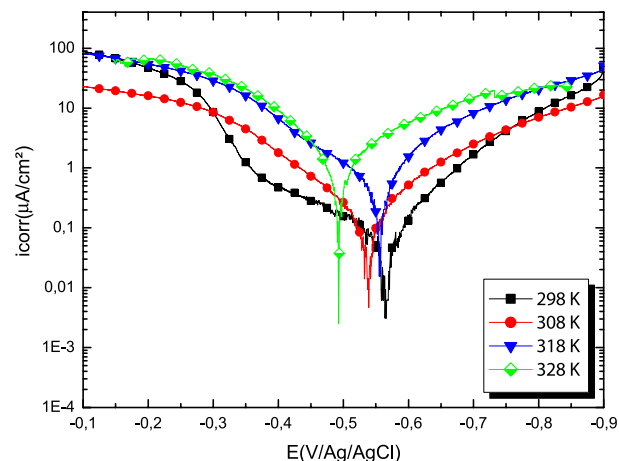


Fig. 8. (Color online) The polarization curves for carbon steel in 1 M HCl in the absence and presence of 200 ppm of LO at different temperatures.

Table 6. Electrochemical carbon steel corrosion in 1 M HCl at different temperatures, in the absence and presence of 200 ppm of LO.

Inhibitor	T (K)	$-E_{\text{corr}}$ (mV/Ag/AgCl)	I_{corr} ($\mu\text{A cm}^{-2}$)	EI (%)
Blank	298	498	470	—
	308	491	800	—
	318	475	1600	—
	328	465	2000	—
LO	298	566	55	88
	308	540	63.6	92
	318	494	100.4	94
	328	491	140.9	93

with a higher speed, the inhibitory efficiency of LO increases with the temperature reaching a maximum value of 94% at 318 K to a concentration of 200 ppm.

The calculation of the parameters of activation for the process of corrosion is realized by using the equations of Arrhenius (12 and 13).²⁹

$$I_{\text{corr}} = A \exp\left(\frac{-E_a}{RT}\right), \quad (12)$$

where

$$\ln(I_{\text{corr}}) = -\frac{E_a}{RT} + \ln(A) \quad (13)$$

E_a is the activation energy (kJ mol^{-1}), R is the ideal gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the absolute temperature (K) and A is the pre-exponential factor.

The state of transition is described by the enthalpy of activation $\Delta H_{\text{ads}}^\circ$ and the entropy of activation ($\Delta S_{\text{ads}}^\circ$) determined from Eqs. (14) and (15).^{30,31}

$$\ln\left(\frac{I_{\text{corr}}}{T}\right) = -\frac{\Delta H_{\text{ads}}^\circ}{RT} + B, \quad (14)$$

$$I_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{\text{ads}}^\circ}{R}\right) \exp\left(\frac{\Delta H_{\text{ads}}^\circ}{R}\right), \quad (15)$$

where h is the Planck constant and N is the Avogadro's number.

Figures 9 and 10, respectively, show the variation of the logarithm of the corrosion current density of $\ln(I_{\text{corr}})$ and $\ln\left(\frac{I_{\text{corr}}}{T}\right)$ carbon steel in HCl alone and in the presence of LO at different concentrations, according to the inverse of the absolute temperature ($1000/T$). We notice that the variations $\ln(I_{\text{corr}}) = f\left(\frac{1}{T}\right)$ and $\ln\left(\frac{I_{\text{corr}}}{T}\right) = f\left(\frac{1}{T}\right)$ are sensibly linear whose coefficient of regression R is of the order of 0.99 (Table 6) that these variations obey the law of Arrhenius in both the absence and presence of LO. Straight lines are obtained with a slope of $\Delta H_{\text{ads}}/R$ and an intercept of $\ln R/Nh + \Delta S_{\text{ads}}/R$. These results allowed us to calculate the apparent activation energy, enthalpies and entropies of dissolution of carbon steel in the absence and presence of our inhibitor.

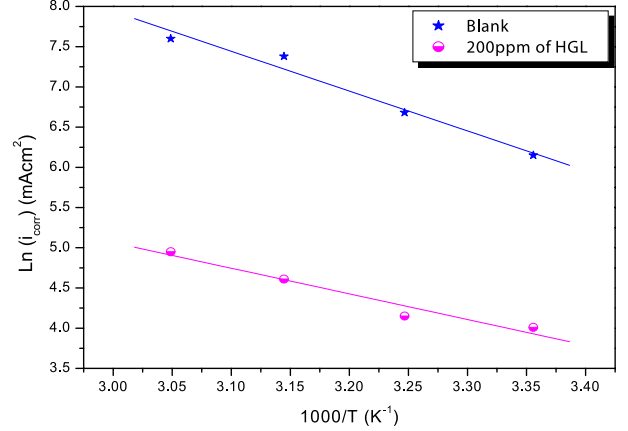


Fig. 9. The right of Arrhenius by the density of the steel corrosion current with and without the addition of 200 ppm of LO.

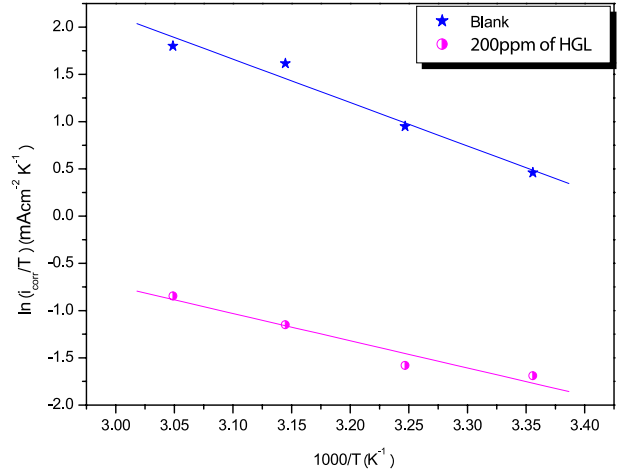


Fig. 10. Variation of $\ln(I_{\text{corr}}/T)$ according to the inverse of the temperature in the absence and presence of 200 ppm of LO.

The values of the thermodynamic parameters relating to the inhibitor determined from Figs. 9 and 10 and those obtained by using Eqs. (13) and (15) are given in Table 7.

Table 7. The values of the activation parameters $\Delta H_{\text{ads}}^\circ$ and $\Delta S_{\text{ads}}^\circ$ for carbon steel in 1 M HCl in the absence and presence of 200 ppm of LO.

Inhibitor	R^2	E_a (KJ · mol ⁻¹)	$\Delta H_{\text{ads}}^\circ$ (KJ · mol ⁻¹)	$\Delta S_{\text{ads}}^\circ$ (J · mol ⁻¹ · K ⁻¹)
Blank	0.999	41	38	275
C_{inh} (200 ppm)	0.999	26	24	209

From the results of Table 7, we notice that

- The values of the activation energy, enthalpy and entropy of the steel dissolution in the presence of LO are lower than those obtained in absence of LO.
- The activation enthalpy obtained from the graph $\ln(I_{\text{corr}}/T) = f(1/T)$ is in good agreement with those found by using Eq. (12). The positive values of this enthalpy indicate that the dissolution process of the steel is endothermic.

The decrease of the activation energy in the presence of LO can be attributed to the chemisorption of the inhibitor on the surface of the carbon steel.^{32–35} The efficiency of the inhibition is due to the nature and the structure of the molecules contained in LO. The latter adsorb on the metallic surface by forming strong connection datives which leads to an adsorption of chemical nature.³⁶ The high and positive values of $\Delta S_{\text{ads}}^{\circ}$ in the presence of LO translate an increase of the disorder during the training of the complex metal-inhibitor.^{37–41}

4. Conclusion

- The main constituents of the oil of linseed, Tricyclo [4.1.0.0 (2,7)]hept-3-ene, oleic acid, 4-methyl-2-pentanol, 1,4-dimethyl benzene, are identified by chromatography in vapor phase coupled with the mass.
- The study of the inhibition of corrosion of the carbon steel in a 1 M HCl solution in the absence and in the presence of LO was done by measures of loss of mass and by electrochemical tests gives the following results.
- The experimental study shows that LO acts as an effective inhibitor corrosion for the carbon steel in acid medium 1 M HCl, and the potential shifting shows that it is about an inhibitor of mixed nature.
- The adsorption of LO on the metallic surface obeys the isotherm of adsorption of Langmuir.
- The mechanism of adsorption of the LO on the carbon steel in a 1 M HCl solution implies the processes of chemisorption at the same time.

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