Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(9):225-238
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

The use of *Pistacia lentiscus* L. oil as green inhibitor for corrosion of mild steel in 1M Hydrochloric acid solution: Thermodynamic and adsorption investigations

Taoufik Haloui[1], Yassine Kharbach[2], Zineb Tribak[2], Mohamed El Azzouzi[3], Abdelouahad Aouniti[3], Belkheir Hammouti[3,4] and Aziz B. Alaoui[1]

[1] *Laboratory of Functional Ecology and Environment, Faculty of Sciences and Technology, Sidi Mohamed Ben Abdellah University, Road Imouzzer. Fez, Morocco*
[2] *Laboratory of Applied Chemistry, Faculty of Science and Technology, Sidi Mohamed Ben Abdellah University, Road Imouzzer. Fez, Morocco*
[3] *Laboratory of Applied Chemistry and Environment.URAC18. Faculty of Sciences, Mohamed 1st University, Oujda 60000, Morocco*
[4] *Petrochemical Research Chair, Department of Chemistry, College of Science, King Saud University, Riaydh 11451, Saudi Arabia*

ABSTRACT

The inhibitory effect of Pistacia lentiscusL. Leaves essential oil was estimated on the corrosion of mild steel in 1M HCl using weight loss, Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curves. Inhibition was found to increase with increasing concentration of P. lentiscusessential oilto attain 90.8 % at 2.56 g/L of (PLL) at 303 K. The effect of temperature on the corrosion behavior of mild steel in 1M HCl with addition of (PLL) was also studied and the process followed the kinetic/thermodynamic model of El-Awady et al. in the temperature range from 303 to 333 K. The calculated ΔG°_{ads} *value showed that the corrosion inhibition of the carbon steel in 1 M HCl is mainlycontrolled by a physisorption process. The results obtained showed that oil of P. lentiscuscould serve as an effective inhibitor of the corrosion of mild steel in Hydrochloric acid medium.*

Keywords: *Pistacia lentiscus*, Essential oil, electrochemical measurements, Adsorption, Mildsteel.

INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals.Corrosion inhibitors are used to reduce the corrosion rates of metallic materials in acidic media [1-3]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen, these compounds can be adsorbed on the steel surface to reduce corrosion attack on steel decreasing the corrosion rate [4,5].

Recently, the strict environmental legislations and increasingecological awareness among scientists have been conducted on the inhibition corrosion of metals by plant extract [6], and essentialoils [7-9].The *Pistacia lentiscus* L. collected from Ifrane's forest at Taounate region in Morocco was selected for this study because it is a cheap plant, environmentally friendly and non-toxic natural compound that could be used for acid pickling of carbon steel in acid medium. The chemical composition ofessential oil of (PLL) has been recently established in our previouswork [10] using gas chromatography (GC) coupled to mass spectrometry GC / MS.

P. lentiscus belong to the family of *Anacardiaceae*, also called mastic tree [11]. It is an evergreen shrub, up to 5 m high. Originally from the Mediterranean basin, the mastic tree is a native species of Morocco [12], which grows on all kinds of soil [13].

The therapeutic properties of this species were known, long time ago. It is used in cosmetics, perfumes and as a flavoring in food preparations [14]. Antibacterial [15,16], anti-fungal [17,18], insecticides [19] and antioxidants [20] effects have been reported for *P. lentiscus* essential oil.

The aim of this study is to evaluate the corrosion inhibition of mild steel in hydrochloric acid by the oil of *P. lentiscus*. The inhibition performance was examined successively via weight loss, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and the isotherms calculations.

MATERIALS AND METHODS

1.1. Extraction and analysis of essential oil

The inhibitor studied namely by *P. lentiscus* leaves were collected from natural populations at the flowering stage during May 2014 in the Ifrane’s forest at Taounate region in Morocco (Altitude: 475 m, 34° 35'12.5" N 4° 38'31.1" W).

P. lentiscus were submitted to hydro-distillation using a Clevenger- type apparatus [21]. Plant material the plant material was extracted in 3 hours. The moisture content of the plant material was determined by drying at 105 ° C for 4 hours [22]. The essential oil is dried over anhydrous sodium sulfate and stored in a glass vial and sealed opaque at 4 ° C in the shade.

The essential oil was analyzed using Gas chromatography (GC) coupled to mass spectrometry GC / MS (Polaris Q ion trap MS), analyses were performed on a Hewlett-Packard (HP 6890) gas chromatograph (FID), equipped with a 5% phenyl methyl silicone HP-5 capillary column (30m x 0.25 mm x film thickness 0.25 µm). The temperature was programmed from 50°C after 5 min initial hold to 200°C at 4°C/min. Gas chromatography were as follows: N2 as carrier gas (1.8 ml/min), split mode was used (Flow: 72.1 ml/min, ratio: 1/50), temperature of injector and detector was 250°C,Final hold time was 48 min.

The machine was led by a computer system type “HP ChemStation”, managing the functioning of the machine and allowing to follow the evolution of chromatographic analyses. Diluted samples (1/20 in methanol) of 1µl were injected manually.

1.2. Materials

Tests were performed on carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) of the following composition0.370 % 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),with a shape and surface dimensions of 1.5 × 1.5 cm was used and pre-treated by grinding with emery paper SiC (120, 600 and 1200). Before use, the carbon steel used was rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature.

The test solutions were prepared by the dilution of analytical grade 37% HCl with distilled water. Inhibitor was dissolved in acid solution at required concentrations and the solution in the absence of inhibitor was taken as blank for comparison purposes.

1.3. Corrosion tests

In this work we used the three classical techniques to determine the corrosion inhibitor characteristics of *P. lentiscus* essential oil in 1 M HCl medium: The weight loss measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves.

Weight loss testing was developed on rectangular specimens with a size of(1.5 cm × 1.7 cm × 0.3 cm). The immersion time was 6 h at room temperature (30 ± 1°C) in 1 M HCl solution with and without addition of different concentrations of *P. lentiscus* essential oil. The weight of each specimen was measured before and after testing using an analytical balance (precision ±0.1 mg).After weighing accurately the specimens were immersed in solutions, at the end of the test, the specimens were taken out, washed carefully and weighed accurately. Triplicate experiments were performed in each case after exposure to 1M HCl solution with and without the addition of various concentrations of *P. lentiscus* essential oil.

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. Potentiodynamic polarization measurements were performed in a conventional three electrode cylindrical Pyrex glass cell. The temperature is thermostatically controlled at 30 ± 1°C. Carbon steel specimen was used as the working electrode, a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The surface area exposed to the electrolyte is 1 cm².

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Voltalab PGZ100 computer at E_{corr} after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after the immersion at 303 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

RESULTATS AND DISCUSSION

1.4. Effect of inhibitor concentration

Values of weight loss based on the weight loss measurements, the corrosion rate C_R and the efficiency η (%) for various concentrations of *P. lentiscus* essential oil, after 6 h of immersion at 303 K in 1M HCl medium were calculated by the following equations [23]and given in Table 1.

$$C_R = \frac{W_b - W_a}{At} \qquad (1)$$

$$\eta(\%) = \left(1 - \frac{w_i}{w_0}\right) \times 100 \qquad (2)$$

Where W_b and W_a are the specimen weight before and after immersion in the tested solution, where w_i and w_0 are the corrosion rates of steel in the absence and presence of the organic compound, respectively.

From Table 1 it could be observed that the values of η (%) were gradually increased with the increase in concentration of *P. lentiscus* essential oil, and they in turn the corrosion rate decreases. At this purpose, one observes that the optimum concentration of inhibitor required to achieve the efficiency is found to be 2.56 g/L (η = 90.8 %). The high inhibition efficiencies values found indicate a strong adsorption (physisorption and/or chemisorption) favored by the long duration of the experiments.

Table 1: Inhibitor efficiencies in 1M HCl solution in presence and absence of different concentrations of *P. lentiscus* essential oil at 6h at 303 K

Concentration (g/L)	C_R (mg.cm^{-2}.h^{-1})	*H* (%)
Blank	1.136	--
2.56	0.103	90.8
2.13	0.128	88.6
1.71	0.180	84.1
1.28	0.248	78.1
0.85	0.301	73.4

1.5. Potentiodynamic measurements

Figure 1 represent the potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of various concentration of *P. lentiscus* essential oil extracts compounds under study.

The values of corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c), corrosion current density (I_{corr}) and percentage inhibition efficiency (η %) are presented in Table 2.

The values of inhibition efficiency (η_{Tafel}%) were calculated using the following equation [24]:

$$\eta_{Tafel}\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (3)$$

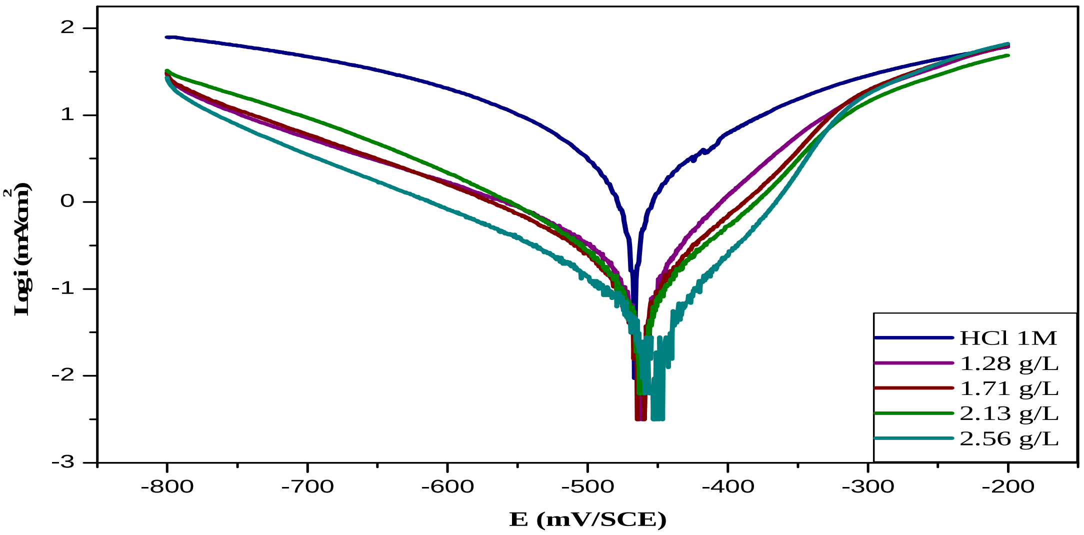

Figure 1: Potentiodynamic polarization curves of mild steel in 1M hydrochloric acid solution containing various concentrations of *P. lentiscus* essential oil

Where I_{corr} and $I_{corr(inh)}$ are the values of corrosion current densities of steel without and with the additive, respectively, which were determined by extrapolation of the cathodic Tafel lines to the corrosion potential E_{corr}.

Table 2: Potentiodynamic polarization parameters of steel at various concentrations of *P. lentiscus* essential oil in 1M HCl and corresponding inhibition efficiencies

	Concentration ($g.L^{-1}$)	E_{corr} (mV/SCE)	β_c (mV/dec)	β_a (mV/dec)	I_{corr} (mA/cm^2)	η (%)
HCl 1M	--	-513.1	-169.3	132.6	0.8111	--
***P. lentiscus* essential oil**	1.28	-461.9	-198.9	89.7	0.3181	60.7
	1.71	-463.1	-174.2	85.7	0.2434	69.9
	2.13	-462.3	-153.9	94.1	0.1518	81.2
	2.56	-453.6	-158.6	82.6	0.0965	88.1

From these results we can conclude that the corrosion densities calculated by Tafel extrapolation decreased with increasing of inhibitor concentrations. This behavior reflects that the compounds of *P. lentiscus* essential oil have an inhibitive effect in the both anodic and cathodic parts of the polarization curves and the addition of essential oil. This means the inhibitor under investigation acts as a mixed type inhibitor.

The corrosion potential of the inhibitor containing solution remains almost unchanged to that in the solution without the essential oil. The slopes of the Tafel line decreases indicating that the inhibition effect is caused by adsorbed inhibiting species [25-27].

1.6. Ac impedance study

The corrosion measures of mild steel in 1M HCl solutions, in absence and presence of various concentrations of *P. lentiscus* essential oil extracts were also investigated by EIS technique. The resultant Nyquist plots are shown in Figure 2. There was a gradual increase in the diameter of each semicircle of the Nyquist plots and this increase of the diameters has clearly shown that the charge transfer resistance R_{ct} values were also increased remarkably as compared to the blank, and that may be due to the formation and gradual improvement in compactness of the barrier layer of the inhibitive molecules adsorbed, and as a result the acid corrosion rates of mild steel were steadily decreased. Various parameters such as polarization resistance (R_{ct}), double layer capacitance C_{dl} and percentage inhibition efficiency (η%) have been calculated and listed in Table 3.

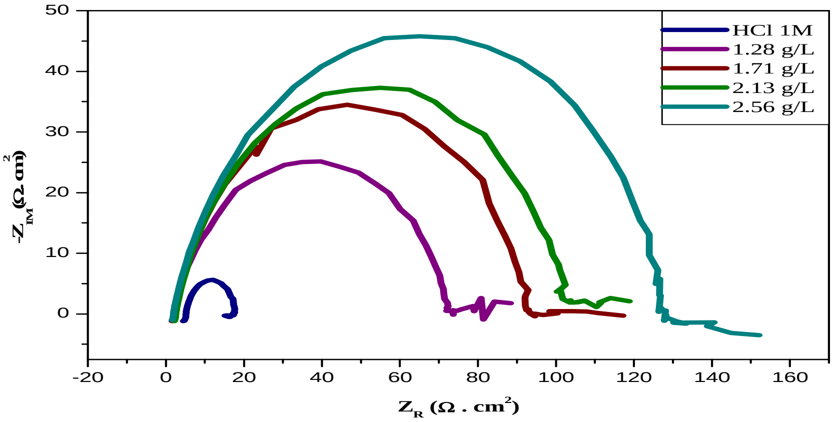

Figure 2: Impedance plot of mild steel obtained in 1M HCl in the absence and presence of various concentrations of *P. lentiscus* essential oil

Data in Table 3 shows that additional *P. lentiscus* essential oil inhibits the corrosion of mild steel in 1 M HCl. The inhibition efficiency is calculated using charge transfer resistance from the equation (4):

$$\eta\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \qquad (4)$$

Where R_{ct} and $R_{ct(inh)}$ are the charge transfer resistance values in absence and presence of inhibition for steel in 1 M HCl, respectively.

By increasing the inhibitor concentration the R_{ct} values increase but C_{dl} values decrease. The calculated ‘‘double layer capacitance” values (C_{dl}), using the following equation [28, 29]:

$$C_{dl} = (AR_{ct}^{1-n})^{1/n} \qquad (5)$$

From Table 3, it was clear that charge transfer resistance R_{ct} values were increased and the capacitance values C_{dl} decreased with increasing inhibitors’ concentration. The decrease in the capacitance which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the *P. lentiscus* essential oil extract act by adsorption at the metal/solution interface [30, 31].

Table 3: Characteristic parameters evaluated from the impedance diagram for steel in 1 M HCl at various concentrations of *P. lentiscus* essential oil

Concentration ($g.L^{-1}$)	R_s ($W.cm^2$)	R_{ct} ($W.cm^2$)	*N*	C_{dl} ($\mu F.cm^{-2}$)	*H* (%)
Blank	2.654	16.29	0.92	152.1	--
1.28	1.882	50.41	0.81	135.1	67.6
1.71	1.982	81.11	0.76	132.4	79.9
2.13	2.316	104.5	0.9	112.1	84.4
2.56	1.783	130.2	0.88	97.71	87.4

1.7. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, generally the corrosion rate increases with the rise of the temperature [32]. For this purpose, the change of the corrosion rate at selected concentrations of the *P. lentiscus* essential oil during 1h of immersion with different temperature 303-343 K was studied in 1M HCl. We made weight loss experiments in the range of temperature 303-343 K, the fractional surface coverage θ can be easily determined from weight loss measurements by the ratio η (%)/100, if one assumes that the values of (η%) do no differ substantially from surface coverage θ. It is clear from Table 4 that the increase of corrosion rate C_R is more pronounced with the rise of temperature for blank solution.

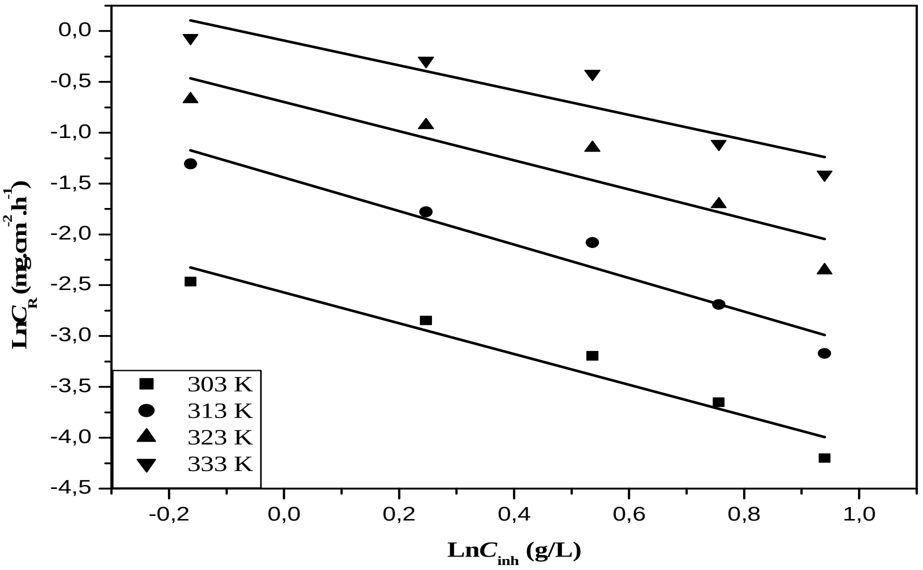

Figure 3: Variation of $\mathrm{Ln}C_R$ with $\mathrm{Ln}C_{inh}$ for mild steel in 1M HCl in absence and presence of *P. lentiscus* essential oil at different temperature

Table 4: Corrosion parameters for mild steel in 1M HCl in absence and presence of optimum concentration of the inhibitor studied *P. lentiscus* essential oil at different temperatures at 1h

Temperature (K)	C_{inh} (g/L)	C_R (mg.cm^{-2}.h^{-1})	H (%)	θ
303	Blank	0.169	---	---
	2.56	0.015	90.8	0.908
	2.13	0.026	84.6	0.846
	1.71	0.041	75.3	0.753
	1.28	0.058	65.3	0.653
	0.85	0.085	49.2	0.492
313	Blank	0.396	---	---
	2.56	0.042	89.1	0.891
	2.13	0.068	82.7	0.827
	1.71	0.125	68.4	0.684
	1.28	0.169	57.3	0.573
	0.85	0.271	31.5	0.315
323	Blank	0.676	---	---
	2.56	0.095	85.8	0.858
	2.13	0.182	73	0.73
	1.71	0.317	52.9	0.529
	1.28	0.396	41.3	0.413
	0.85	0.511	24.3	0.243
333	Blank	1.092	---	---
	2.56	0.244	77.6	0.776
	2.13	0.33	69.7	0.697
	1.71	0.658	39.7	0.397
	1.28	0.747	31.5	0.315
	0.85	0.936	14.3	0.143

Table 4 shows that the data obtained suggest that essential oil get adsorbed on the steel surface at all temperatures studied and corrosion rates increased in absence and presence of inhibitor with increase in temperature in 1M HCl solutions.

In acidic media, corrosion of metal is generally accompanied with evolution of H_2 gas; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal.

Assuming that the corrosion rate of mild steel against the concentration of the studied inhibitor obeys the following kinetic relationship [33,34].

$$\mathrm{Ln}C_R = B\mathrm{Ln}C_{inh} + \mathrm{Ln}k \qquad (6)$$

Where k is the rate constant and equal to C_R at inhibitor concentration of unity, B is the reaction constant which in the present case is a measure of the inhibitor effectiveness, and $C_{inh}$is the inhibitor concentration table 5.

Table 5: Kinetic parameters for the corrosion of mild steel in 1M HCl containing *P. lentiscus* essential oil

Temperature (K)	B	k ($mg.cm^{-2}.h^{-1}$)
303	-1.511	0.910
313	-1.648	0.497
323	-1.432	0.236
333	-1.219	0.076

1.8. Corrosion kinetic study

To calculate activation thermodynamic parameters of the corrosion process, we are using the Arrhenius equation (7) and transition state equation (8) in the temperature range from 303 to 343 K [35]:

$$C_R = A exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

$$C_R = \frac{RT}{Nh} exp\left(\frac{\Delta S_a}{R}\right) exp\left(-\frac{\Delta H_a}{RT}\right) \qquad (8)$$

Where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is Plank's constant, N is Avogrado's number, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

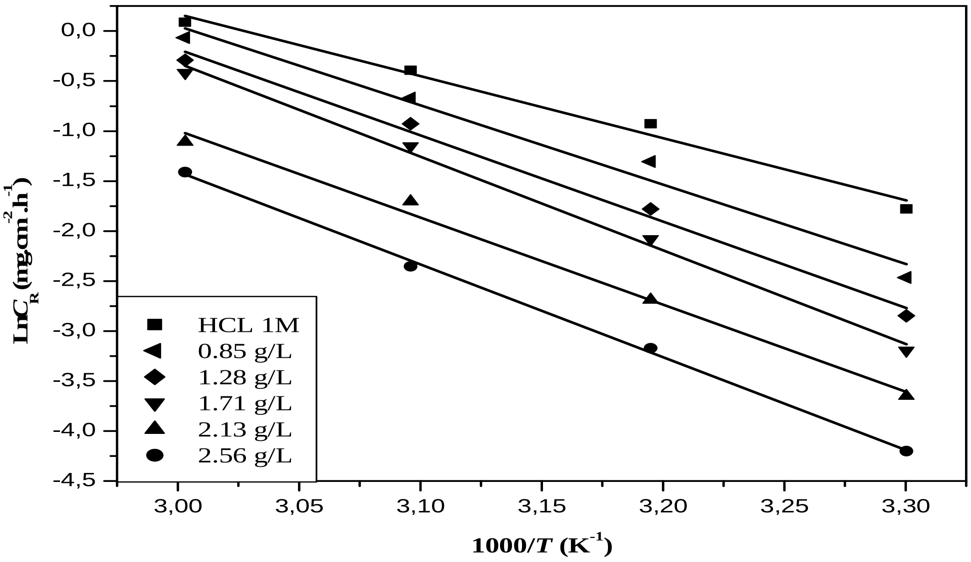

Figure 4: Arrhenius plots for mild steel corrosion rates (C_R) in 1M HCl containing *P. lentiscus* essential oil

Table 6: Kinetic-thermodynamic corrosion parameters for mild steel in 1M HCl in absence and presence of different concentrations of *P. lentiscus* essential oil

C_{inh} (g/L)	E_a ($kJ.mol^{-1}$)	ΔH_a ($kJ.mol^{-1}$)	ΔS_a ($J.mol^{-1}.K^{-1}$)	E_a-ΔH_a
Blank	51.61	48.97	-97.42	2.6390
2.56	65.95	63.31	-55.39	2.6398
2.13	71.64	69.01	-40.23	2.6398
1.71	77.81	75.17	-22.88	2.6398
1.28	72.35	69.71	-44.88	2.6390
0.85	77.04	74.40	-45.61	2.6398

Arrhenius plots for the corrosion rate of mild steel are given in Figure 4. Values of apparent activation energy of corrosion (E_a) form ild steel in 1M HCl with the absence and presence of various concentrations of essential oil were determined from the slope of Ln(C_R)versus 1/T plots and shown in Table 6. It can be seen from the table 6 that the E_a increased with increasing concentration of essential oil, but all values of E_a in the range of the studied concentration, were higher than that of the uninhibited solution (blank). The increase in E_a in the presence of essential oil may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the inhibited solution is associated with physical adsorption or weak chemical bonding between the inhibitor species and the steel surface [36,37]. It can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with the increase in temperature. A corresponding increase in the corrosion rate occurs because of the greater area of metal that is consequently exposed to the acid environment [38].

Figure 5 shows a plot of Ln(C_R/T) against 1/T. Straight lines are obtained with a slope of (ΔH_a/R) and an intercept of (Ln R/Nh + ΔS_a/ R) from which the values of ΔH_a and ΔS_a are calculated, are listed in Table 6. These data reveals that the ΔH_a values for dissolution reaction of mild steel in 1 M HCl in the presence of essential oil are higher (74.4–63.3 kJ mol^{-1}) than that of in the absence of inhibitors (48.9 kJ mol^{-1}). The positive signs of ΔH_a reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [39] in the presence of inhibitor. One can notice that E_a and ΔH_a values vary in the same way. This result permits to verify the known thermodynamic reaction between the E_a and ΔH_a as shown in Table 7 [40]:

$$\Delta H_a = E_a - RT \qquad (9)$$

Concerning the entropy of activation ΔS_a, it is clear from table 6 that the value of ΔS_a increases with increasing essential oil concentrations, while a negative value is observed in uninhibited solution. The increase of ΔS_a is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes [41]. This observation is in agreement with the findings of other workers [42-45]. This behavior can also be explained as a result of their placement process of water molecules during adsorption of molecule inhibitor on the steel surface and therefore the increasing in entropy of activation was attributed to the increasing in solvent entropy [46].

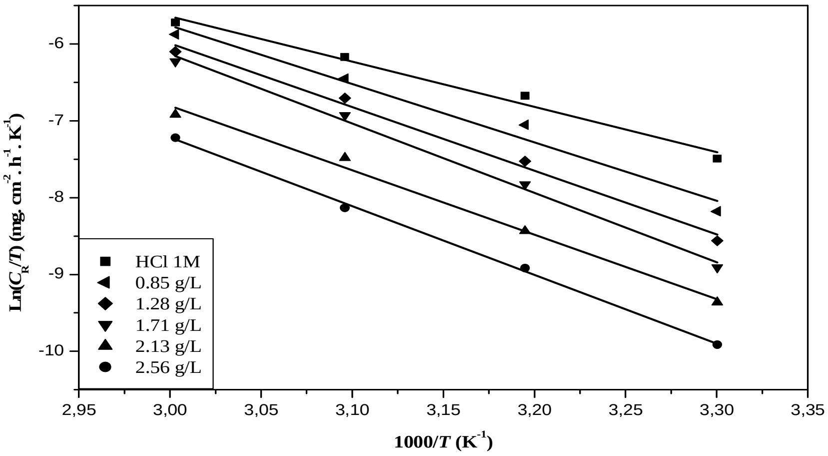

Figure 5: Transition-state plots for mild steel corrosion rates (C_R) in 1M HCl in absence and in presence of different concentrations of *P. lentiscus* essential oil

1.9. Thermodynamic adsorption parameters

If it is assumed, that adsorption of the organic molecules or ions on the metal surface is the cause for the inhibitor action in both acid media, then the surface coverage θ can be estimated using from the inhibitor efficiency as θ = (η%)/100 (table 4) [47].An attempt was made to find a suitable adsorption isotherm, which can describe the concentration dependence of the inhibitor efficiency. As it is known that the adsorption of an organic adsorbate onto metal–solution interface can be presented as a substitutional adsorption process between the organic molecules in the aqueous solution $Org_{(sol)}$ and the water molecules on the metallic surface $H_2O_{(ads)}$:

$$Org_{(sol)} \quad + \quad nH_2O_{(ads)} \leftrightarrow Org_{(ads)} \quad + \quad nH_2O_{(sol)} \qquad (10)$$

Where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ is the water molecules on the metallic surface, n is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate. When the equilibrium of the process described in this equation is reached, it is possible to obtain different expressions of the adsorption isotherm plots, and thus the surface coverage degree (θ) can be plotted as a function of the concentration of the inhibitor under test [48].

The experimental data are most often described by the adsorption isotherms of Langmuir, Frumkin or Temkin. Best fit was obtained with the Temkin adsorption isotherm [49]:

$$f\theta = \text{Ln K} + \text{Ln C}_{\text{inh}} \qquad (11)$$

Where C_{inh} is the inhibitor concentration in the electrolyte and *K*is the equilibrium constant of the adsorption process.

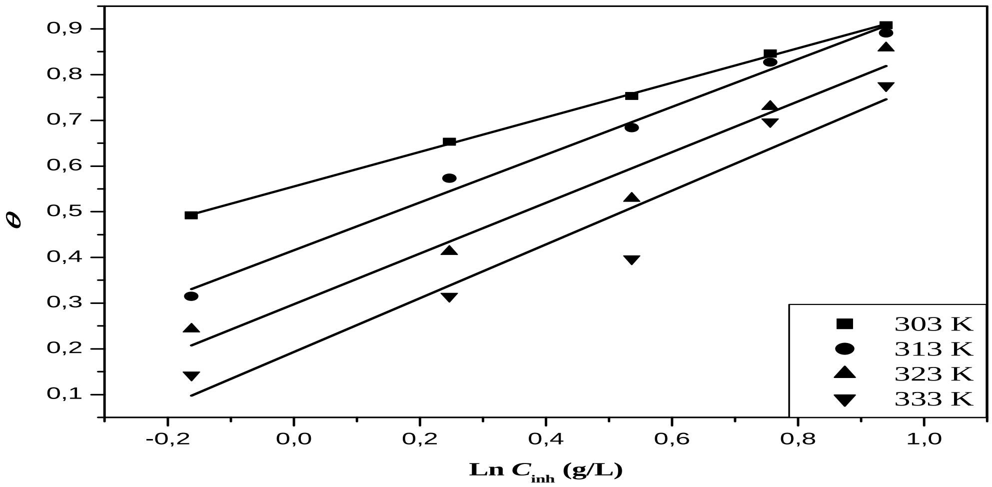

Figure 6: Temkin's isotherm adsorption model of *P. lentiscus* essential oil on the mild steel in 1M HCl

Table 7: Adsorption parameters for *P. lentiscus* essential oil in 1M HCl obtained from Temkin adsorption isotherm at different temperature

T°	R^2	Slope
303	0.9993	0.378
313	0.9918	0.522
323	0.9676	0.554
333	0.9308	0.588

The experimental points and calculated isotherm line are plotted in Figure6. A very good fit is observed with the regression coefficients up to 0.9, which suggests that the experimental data are well described by Temkin isotherm. However, the deviation of the slope from unity showed that the isotherm cannot be strictly applied. Hence, the experimental data were fitted into the El-Awady's kinetic/thermodynamic model. The characteristic of the isotherm is given by [50]:

$$Ln\frac{\theta}{1-\theta} = LnK + yLnC_{inh} \qquad (12)$$

Where C_{inh} is the molar concentration of inhibitor, *θ*is the degree of surface coverage, *K* is a constant related to the equilibrium constant of the adsorption process, K_{ads}, by the following relationship:

$$K_{ads} = K^{\frac{1}{y}} \qquad (13)$$

Where *y* is the number of inhibitor molecules occupying one active site and 1/*y* represents the number of active sites of the metal surface occupied by one molecule of inhibitor.

The plot showing in Figure 7 gave straight lines which clearly showed that the data fitted well to the isotherm. The values of 1/*y* and K_{ads} calculated from the El-Awady et al. model curve is given in table 8.The decreasing value of K_{ads} with increase in temperature indicates that adsorption of *P. lentiscus* essential oil on the mild steel surface was unfavorable at higher temperatures. K_{ads} is related to the standard Gibbs energy of adsorption, $\Delta G°_{\text{ads}}$, according to [51]. The calculated $\Delta G°_{\text{ads}}$ values, using equation (14), were given in Table 6.

$$K_{ads} = \frac{1}{C_{H_2O}} exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (14)$$

Where *R* is the universal gas constant, *T* the thermodynamic temperature and the concentration of water in the solution is 1000 g/l.

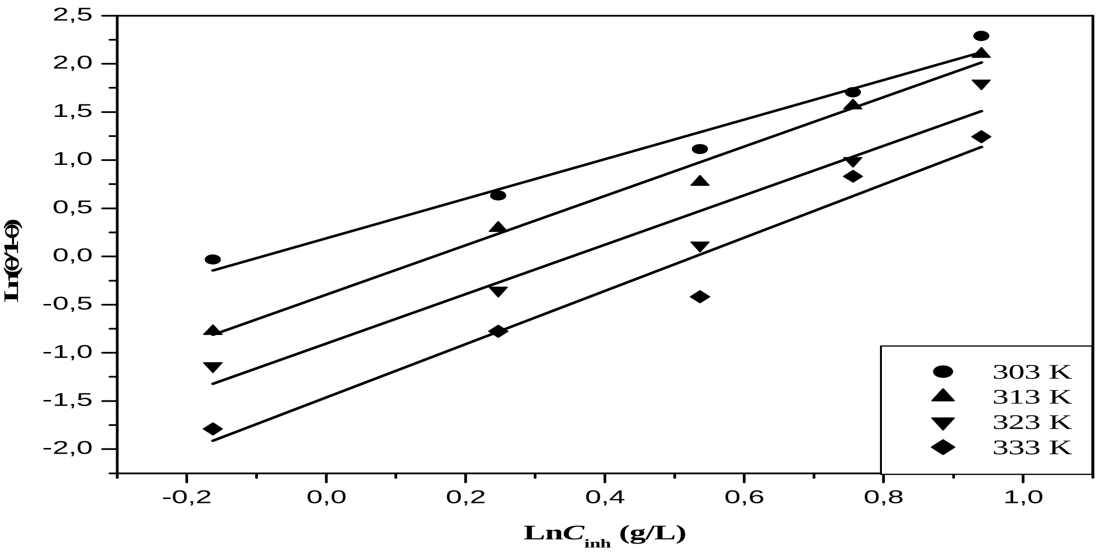

Figure 7: El-Awady's isotherm adsorption model of *P. lentiscus* essential oil on the mild steel surface in 1M HCl at different temperatures

Table 8: Calculated parameters for El-Awady adsorption isotherm in the presence of *P. lentiscus* essential oil in 1 MHCl at different temperatures

Temperature (K)	K (g/L)	$1/y$	K_{ads} (g/L)	$\Delta G°_{ads}$ (kJ.mol^{-1})	R^2
303	1.2	0.48	1.09	-10.33	0.9761
313	0.63	0.39	0.83	-9.96	0.9889
323	0.4	0.38	0.71	-9.86	0.9516
333	0.23	0.36	0.58	-9.61	0.957

$\Delta G°_{ads}$ values were found to be up to-20 kJ mol^{-1}(Table 8) indicating the spontaneity of the adsorption process at the surface of N80 steel. Values of $\Delta G°_{ads}$ around -20 kJ/mol or lower are consistent with the electrostatic interaction between charged organic molecules and the charged metal surface (physisorption), those around -40 kJ/mol or higher involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorptions). The values of $\Delta G°_{ads}$ for *P. lentiscus* essential oil were found to be between (-10.33 kJ/mol) and (-9.61 kJ/mol) indicated that the adsorption mechanism of essential oil on mild steel in 1MHCl solution at the studied temperatures is physisorption [52].$\Delta G°_{ads}$ is related to the standard enthalpy and entropy of the adsorption process, $\Delta H°_{ads}$ and $\Delta S°_{ads}$, respectively, via equation (15):

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (15)$$

A plot of $\Delta G°_{ads}$ vs. T gives straight lines (Figure 8) with the slope equal to - $\Delta S°_{ads}$, and the value of $\Delta H°_{ads}$ can be calculated from intercept (Table 9).

Table 9: Thermodynamic parameters for the adsorption of *P. lentiscus* essential oil on mild Steel in 1M HCl at different temperatures

	Method 1		Method 2		Method 3	
Temperature (K)	$\Delta H°_{ads}$ (kJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})	$\Delta H°_{ads}$ (kJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})	$\Delta H°_{ads}$ (kJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})
303	-17.12	-22.6	-17.21	-22.85	-17.2	-22.67
313						-23.13
323						-22.72
333						-22.79

The $\Delta H°_{ads}$value is negative, suggesting that the adsorptions of inhibitor molecules onto the mild steel surface are an exothermic process.

And the standard enthalpy of adsorption $\Delta H°_{ads}$ can be calculated according to the Van't Hoff equation (Method2) [53]:

$$LnK_{ads} = -\frac{\Delta H^{\circ}_{ads}}{RT} + constant \qquad (16)$$

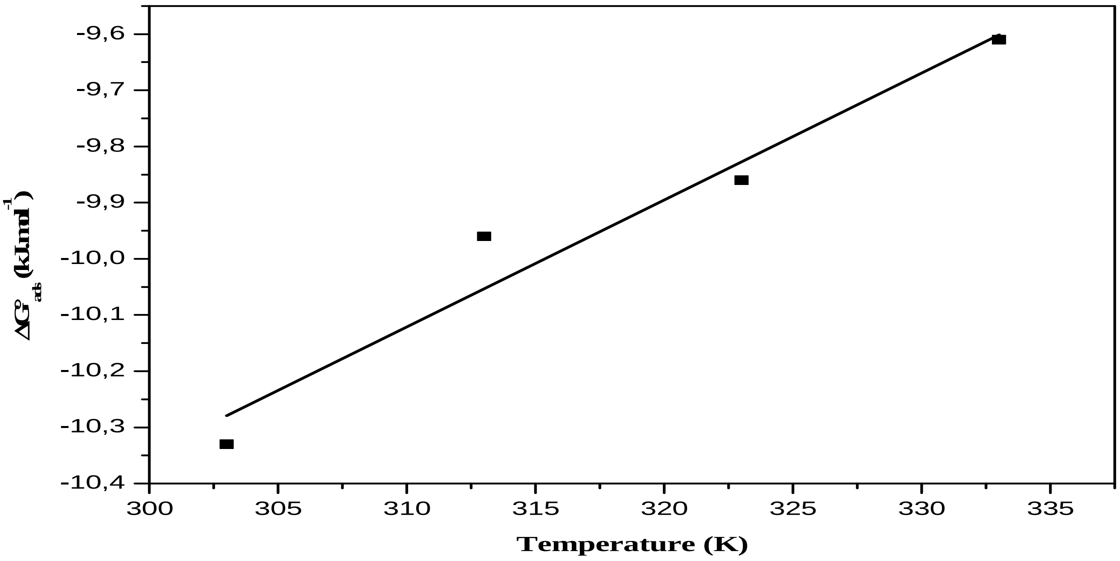

Figure 8: Variation of $\Delta G°_{ads}$ versus *T* on mild steel in 1M HCl containing *P. lentiscus* essential oil

A plot of Ln K_{ads} versus $1/T$ gives a straight line, as shown in Figure 9. The slope of the straight line is - $\Delta H°_{ads}/R$ and the intercept is ($\Delta S°_{ads}/R$ + $\ln 1/C_{H2O}$). The obtained values of $\Delta H°_{ads}$ and $\Delta S°_{ads}$ are given in Table 9.

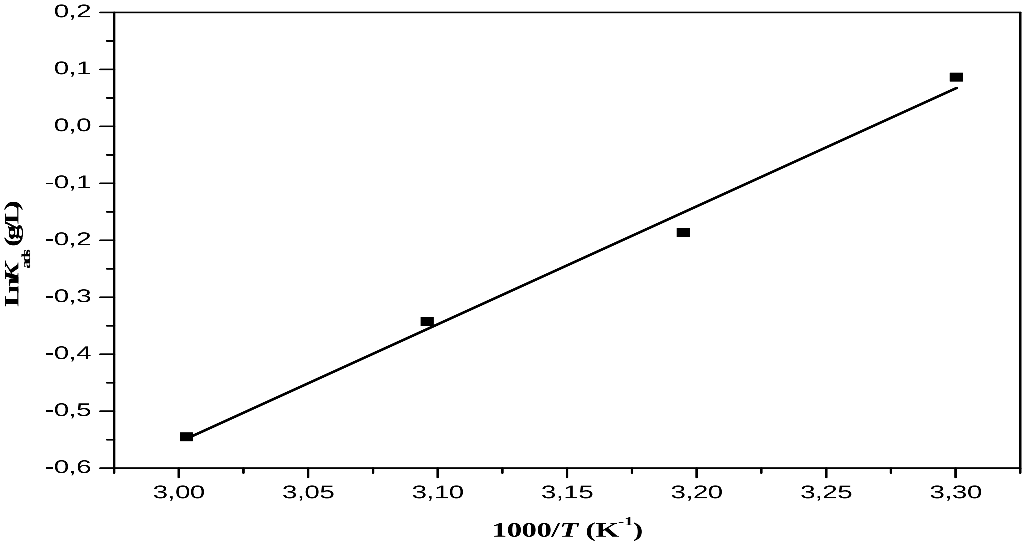

Figure 9: Van't Hoff plot for the mild steel/ *P. lentiscus* essential oil /1 M HCl system.

The thermodynamic parameters ($\Delta H°_{ads}$and $\Delta S°_{ads}$) can also evaluated using the Gibbs-Helmholtz equation (Method 3), which is defined as follow [54]:

$$\left[\frac{\partial\left(\Delta G^{\circ}_{ads}/T\right)}{\partial T}\right]_{p} = -\frac{\Delta H^{\circ}_{ads}}{T^{2}} \qquad (17)$$

Equation (17) can be arranged to give the following equation:

$$\frac{\Delta G^{\circ}_{ads}}{T} = -\frac{\Delta H^{\circ}_{ads}}{T} + constant \qquad (18)$$

$\Delta H°_{ads}$ and $\Delta S°_{ads}$ for the adsorption of oil on steel surface can be also deduced from equation (15). Figure 10 shows the plot of $\Delta G°_{ads}$/T versus 1000/T which gives straight lines with slopes. The obtained value of $\Delta H°_{ads}$ was -□□ kJ mol^{-1}. In this case, the values of $\Delta H°_{ads}$ and $\Delta S°_{ads}$ obtained by the three methods are in good agreement (Table 9).

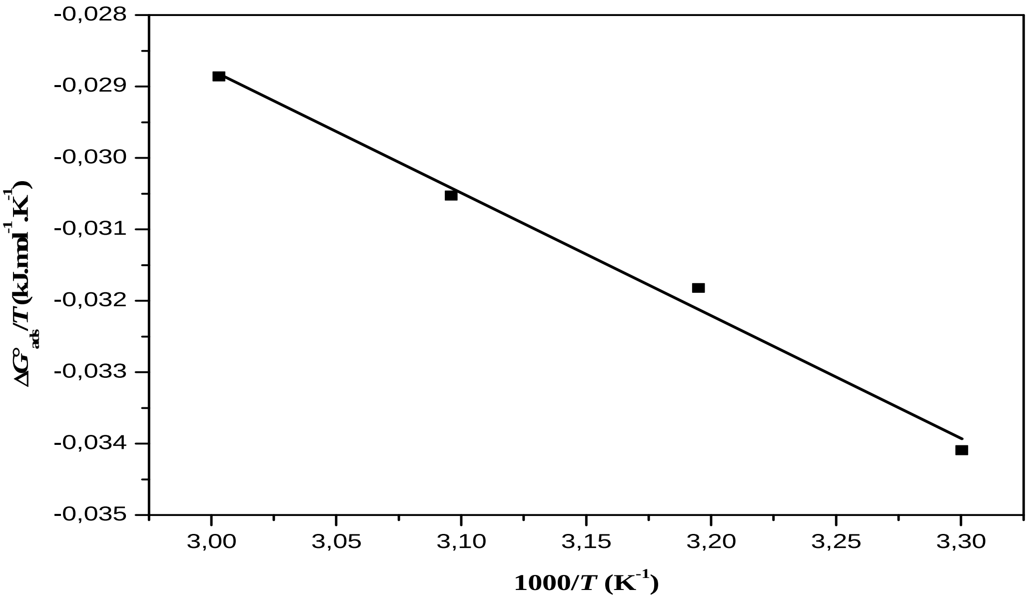

Figure10: Relationship between □$G°_{ads}/T$ and the reverse of absolute temperature

1.10. **Essential** *oil composition*

The results of chromatographic analysis of *Pistacia lentiscus* leaves essential oils are presented in Table 10:

Table 10: Main constituents (%) of *Pistacia lentiscus* L. leaves essential oil

RI (min) [a]	Compound [b]	Leaves (%)
915	Tricyclene	7.71
953	Camphene	1.65
974	Sabinene	6.96
1006	α- Phellandrene	2.61
1011	3-carene	4.44
1026	p-Cymene	5.04
1050	trans-β-Ocimene	3.89
1072	γ-Terpinene	0.63
1089	p-Cymenene	0.59
1180	Terpinen-4-ol	7.44
1192	α-Terpineol	4.16
1219	Trans- Carveol	0.62
1266	Geraniol	0.58
1288	Bornyl acetate	3.32
1294	Undecanone	0.80
1348	α-Cubebene	1.06
1381	α-Copaene	0.83
1395	β-Elemen	0.94
1418	Caryophyllene	6.62
1454	α-Caryophyllene	1.65
1462	Benzoic acid, pentyl ester	0.57
1464	Aromadendrene	0.65
1499	α-Muurolene	1.83
1513	γ-Cadinene	0.68
1523	Calamenene	0.80
1528	δ-Cadinene	1.97
1538	α-Cadinene	1.90
1581	Caryophyllene oxide	6.05
1652	α-Cadinol	2.72

a: Retention index.
b: Compounds present in trace amounts (<0.5%) were not registered.

CONCLUSION

The *P. lentiscus* essential oil compounds inhibit effectively the corrosion of mild steel in 1M HCl. Indeed, the optimum percentage of inhibitor required to achieve the efficiency is found to be 90.8%.

The polarization curves indicate that the *P. lentiscus* essential oil as mixed type inhibitor and the impedance data indicate that inhibition was achieved via adsorption. Double layer capacitances decreases with respect to the blank solution when *P. lentiscus* essential oil is added. This fact may be explained on the basis of adsorption of essential oil compounds on the steel surface. In determining the corrosion, electrochemical studies and weight loss measurements give similar results.

The inhibition efficiency of essential oil is found to decrease proportionally with increasing temperature 303-343 K and its addition to 1M HCl leads to increase of apparent activation energy E_a of corrosion process. The corrosion process is inhibited by the adsorption of *P. lentiscus* essential oil on steel surface and the adsorption of the inhibitor fitsa El-Awady's kinetic/thermodynamic model under all of the studied temperatures.

REFERENCES

[1] J.M. Sykes, *Br.Corros. J.*, **1990**, 25, 175-183.
[2] L.F. Guo, D.M. Zhang, J. Q. Meng, *Acta. Phys.Chim. Sin.*, **2008**, 24, 138.
[3] A. Chetouani, M. Daoudi, B. Hammouti, T. Ben Hadda, M. Benkaddour, *Corros. Sci.*, **2006**, 48, 2987.
[4] F. Bentiss, M. Outirite, M. Traisnel, H. Vezin, M. Lagrenée, B. Hammouti, S.S. Al- Deyab, C. Jama, *Int. J. Electrochem. Sci.*, **2012**, 7, 1699-1721.
[5] M. Lagrenée, B. Mernari, M. Bouanis, M. Taisnel, F. Bentiss, *Corros. Sci.*, **2002**, 44, 573-588.
[6] EH. El-Ashry, A. El-Nemir, SA. Esawy, S. Ragab, *Electrochim. Acta*, **2006**, 51, 3957.
[7] K. Boumhara, F. Bentiss, M. Tabyaoui,J. Costa, J.M. Desjobert, A. Bellaouchou, A. Guenbour,B. Hammouti, S.S. Al-Deyab,*Int. J. Electrochem. Sci.*, **2014**, 9,1187-1206.
[8] Z. Faska, L. Majidi, R. Fihi, A. Bouyanzer, B. Hamouti, *Pigm. Resin Technol.*, **2007**, 36, 293.
[9] A. Bouyanzer, L. Majidi, B. Hammouti, *Phys. Chem. News.*, **2007**, 37, 70.
[10] T. Haloui, M. Fadil, S. Jennan, A. Farah, A. Belrhiti Alaoui, *J. Mater. Environ. Sci.*, **2015**, 4, 942-948.
[11] M. Hmamouchi ; Les plantes médicinales et aromatiques marocaines : utilisations traditionnelles, marchés, biologies, écologies, chimie, pharmacologie, toxicologie, lexiques *Imp. de Fédala*, **1999**, 1, 140.
[12] A. Aafi, M. S. Taleb, M. Fechtal; Espèces, remarquables de la flore du Maroc. Maroc: Centre National de la Recherche Forestière, **2002**, 34.
[13] E. Bayer, K. P. Buttler, X. Finkenzeller, J. Grau ; Guide de la flore méditerranéenne : Caractéristiques, habitats, distribution et particularités de 536 espèces. éd. *Nature Delachaux et Niestlé*, **2009**, 94.
[14] D. Daferera, C. Pappas, P.A. Tarantilis, M. Polisiou,*Food Chemistry.*, **2002**, 77, 511-515.
[15] D. Djenane, J. Yangüela, L. Montañés, M. Djerbal, P. Roncalés, Antimicrobial activity of *Pistacia lentiscus*and *Satureja montana* essential oils against Listeria monocytogenes CECT 935 using laboratory media: Efficacy and synergistic potential in minced beef. Food Control, **2011**, 22, 1046-1053.
[16] T. Haloui, A. Farah, M. Balouiri, M. Chraibi, M. Fadil, K. F. Benbrahim, A. B. Alaoui, *J. Appl.Pharm. Sci.*, **2015**, 5 (6), 50-53.
[17] M. E. Duru, A. Cakir, S. Kordali, H. Zengin, M. Harmandar, S. Izumi, T. Hirata,*Fitoterapia.*, **2003**, 74, 170–176.
[18] S. Kordali, A. Cakir, H. Zengin, M. E. Duru,.*Fitoterapia.*, **2003**, 74, 164–167.
[19] O. Bachrouch, J. M. Ben Jemâa, W. Aidi, T. Thierry, M. Brahim, A. Manef, *Bulletin of Insectology.*, **2010**,63(1), 129-135.
[20] A.Barra, V. Corneo, S. Dessi, P. Cabras, A. Angioni, *J. Agric. Food Chem.*, **2007**, 55, 7093-7098.
[21] S. Zrira, B. Benjilali, G. Lamaty,*Actes Inst Agron Veto- Maroc.*, **1995**, 15(4), 27-35.
[22] J. F. Clevenger, *J. Am. Pharm. Assoc.*, **1928**, 17, 341-6.
[23] K. Boumhara, F. Bentiss, M. Tabyaoui, J. Costa, J. M. Desjobert, A. Bellaouchou, A. Guenbour, B. Hammouti, S. S. Al-Deyab, *Int. J. Electrochem. Sci.*, **2014**, 9, 1187–1206.
[24] H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama, F. Bentiss, *Corros. Sci.*, **2012**, 64, 243–252.
[25] M.B. Cisse, B. Zergar, F. El Kalai, M. Ebn Touhami, M. Sfaira, M. Taleb, B. Hammouti, N. Benchat, S. El Kadiri, A. Touimi Benjelloun, *Surf. Rev. Lett.*, **2011**, 18, 303.
[26] B. Zerga, B. Hammouti, M. Ebn Touhami, R. Touir, M. Taleb, M. Sfaira, M. Bennajeh, I. Forssal, *Int. J. Electrochem. Sci.*, **2012**, 7, 471.
[27] F. Bentiss, C. Jama, B. Mernari, H. El Attari, L. El Kadi, M. Lebrini, M. Traisnel, M. Lagrenée, *Corros. Sci.*, **2009**, 51, 1628.
[28] H. Ma, X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, L. Niu, *Corros. Sci.*,**2000**, 42, 1669.

[29] A. Popova, M. Christov, A. Vasilev, *Corros. Sci.*, **2007**, 49, 3290.
[30] H. Bouammali, A. Ousslim, K. Bekkouch, B. Bouammali, A. Aouniti, S. S. Al-Deyab, C. Jama, F. Bentiss,B. Hammouti,*Int. J. Electrochem. Soc.*, **2013**, 8, 6005-6013.
[31] O. Benali, L. Larabi, M. Traisnel, L. Gengembre, Y. Harek, *Appl. Surf. Sci.*, **2007**, 253, 6130.
[32] F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.*, **2005**, 47, 2915.
[33] E. Khamis, M.A. Ameer, N.M. Al-Andis, G. Al-Senani, *Corrosion*, **2000**, 56, 127.
[34] E. A. Noor, *Corros. Sci.*, **2005**, 47, 33.
[35] J. O. M.Bockris, A. K. N. Reddy, Modern Electrochemistry, Plenum Press, New York, **1977**, 2, 1267.
[36] A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.*, **2003**, 45, 33.
[37] M. Elayyachy, M. Elkodadi, A. Aouniti, A. Ramdani, B. Hammouti, F. Malek, A. El idrissi, *Mat. Chem. Phys.*, **2005**, 93, 281.
[38] T. Szauer, A. Brand, *Electrochim. Acta.*, **1981**, 26, 1219.
[39] N. M. Guan, L. Xueming, L. Fei, *Mater. Chem. Phys.*, **2004**, 86, 59.
[40] M. K. Gomma, M. H. Wahdan, *Mater. Chem. Phys.*, **1995**, 39, 209.
[41] L. Herrag, B. Hammouti, S. Elkadiri, A. Aouniti, C. Jama, H. Vezin, F. Bentiss, *Corros. Sci.*, **2010**, 52, 3042.
[42] E. A. Noor, A. H. Al-Moubarak, *Corros. Sci.*, **2009**, 51, 868.
[43] I. Ahamad, R. Prasad, M. A. Quraishi, *Corros. Sci.*, **2010**, 52, 933.
[44] A. Popova, M. Christov, A. Vasilev, *Corros. Sci.*, **2007**, 49, 3276.
[45] M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, *Mater. Lett.*, **2006**, 60,1901.
[46] B. Ateya, B. E. El-Anadouli, F. M. El-Nizamy, *Corros. Sci.*, **1984**, 24, 509.
[47] F. Bentiss, B. Mernari, M. Traisnel, H. Vezin, M. Lagrenée, *Corros. Sci.*, **2011**, 23, 487–495.
[48] N. Labjar, F. Bentiss, M. Lebrini, C. Jama, S. El hajjaji, *Inter. J. Corros.*, **2011**, Article ID 548528.
[49] M. Hosseini, S. F. Mertens, M. Ghorbani, M. R. Arshadi, *Mater. Chem. Phys.*, **2003**, 78, 800-808.
[50] A. El Awady, A. Abd El Naby, S. Aziz, *J. Electrochem. Soc.*, **1992**, 139, 2149.
[51] A.K. Singh, M.A. Quraishi, *Corros. Sci.*, **2011**, 53, 1288.
[52] M. Outirite, M. Lagrenée, M. Lebrini, M. Traisnel, C. Jama, H. Vezin, F. Bentiss, *Electrochim. Acta.*, **2010**, 55, 1670.
[53] M. Bouklah, B. Hammouti, M. Lagrenée, F. Bentiss, *Corros. Sci.*, **2006**, 48, 2831.
[54] S. Bilgic, *Mater. Chem. Phys.*, **2002**, 76, 52.