Research Article

Study of the inhibitory activity of the essential oil of *Myrtus communis* against copper corrosion in a nitric acid medium

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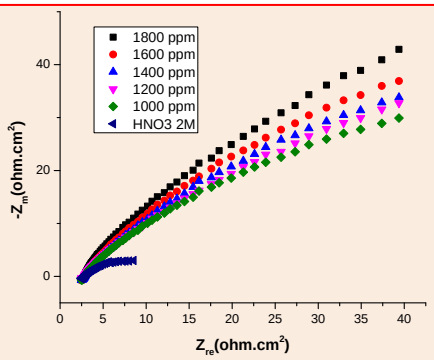
Abstract

The inhibitory action of the essential oil of Myrtus on copper corrosion in a 2 M HNO_3 solution in a temperature range from 283 to 313 K was measured by using the weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The results obtained show that the oil inhibits the corrosion of copper in a solution of 2M HNO_3 and that the effectiveness of the inhibition increases with an increase of the concentration of the inhibitor, and decreases proportionally with a decrease in temperature. It appears from the potentiodynamic polarization studies, that inhibitor is anodic. The dissolution kinetics data were studied.

Keywords: Copper corrosion inhibition, the essential oil of Myrtus, adsorption



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Introduction

Corrosion is a phenomenon of degradation of the metallic materials by the environment. This is a phenomenon that concerns most industrial sectors including aerospace, automotive, and chemical and petrochemical industries. The economic stakes are considerable. Corrosion is not only wasteful of raw materials and energy; it can also cause some serious accidents and often contribute to environmental pollution.

In terms of protection, the use of organic inhibitors is a considerable mean of protection against metal corrosion. However, most of these compounds are toxic and have side effects on human health [1-7]. This is why in latest decades several studies have focused on the use of ecological or green inhibitors. Their advantages are important as to the inhibitory effectiveness required by these compounds, their production cost and the non-toxicity of their compositions. As part of our laboratory program, we are interested in the study of the natural extracts of essential oils such as corrosion inhibitors. In our previous work, we have tested and found an effective inhibitory activity of the extracts of thyme [8, 9], sagebrush [10], castor [11], spearmint [12], verbena [13], clove [14], etc.

In this work, we are interested in the study of the corrosion of the inhibition of copper by Myrtle's essential oil from *Myrtaceae's* family, using gravimetric and electrochemical methods (stationary and transient). The effect of varying the concentration of the inhibitor and the medium temperature was evaluated. At the same time we examined the morphology of the copper's surface h using the scanning electron microscopy (SEM) tool.

Experimental

Essential oil extraction of the Myrtus communis species

The essential oil of this species belonging to the Myrtaceae family was obtained by steam distillation of water using a Clevenger-type distiller for 3 h. The yield of essential oil is 0.87%. The essential oil yield was calculated based on the dry matter. After extraction, a portion of the oil was used for the analysis of the chemical composition by the

technique of gas chromatography coupled by mass spectrometry. The other part was used for testing of anti corrosion activity. The oil obtained after extraction, was covered and saved in a dark bottle and stored at 4°C before use.

Preparation of the solution

The HNO_3 2 M solution was prepared by dilution of the nitric acid of 67% of analytical purity with distilled water. Test solutions were freshly prepared before each experiment by adding the oil directly to the etching solution. Experiments were conducted in triplicate to allow determination of reproducibility.

Gravimetric measurements

Gravimetric tests were carried out maintaining the desired temperature of the electrolyte with a FRIGITHERM thermostat. The electrolyte volume is 30 mL. The samples are in a rectangular area of 9.6 cm^2. Prior to measurements, they undergo a mechanical polishing with abrasive paper of increasing particle size up to 1200, followed by a degreasing with acetone, and then a washing with distilled water and finally air drying. Each value of the gravimetric test is the average of at least three tests.

Electrochemical measurements

The electrochemical experiments were performed in a pyrex cell, equipped with a conventional three-electrode: copper as shaped working electrode of disc cutter with a geometric area of 1 cm^2, the auxiliary electrode and platinum as an electrode and ECS saturated calomel as a reference electrode. The copper disc was abraded with sandpaper to different particle size up to 1200, degreased with acetone, rinsed with distilled and dried before each test water. The measurements are taken with an assembly comprising a potentiostat-galvanostat PGZ100 type radiometer, associated with "*voltamaster4*" software.

The current-potential curve is obtained by the potentiodynamic method; the potential applied to the sample varies continuously with a scanning rate of 30 mV/ min. We chose a relatively low scan rate in order to be at quasi-stationary regime. Before drawing the curves, the working electrode is maintained at a potential of -800 mV for 15 minutes. The measuring of the electrochemical impedance spectroscopy (EIS) was performed with the same electrochemical system. Frequencies between 100 kHz and 10 Hz were superimposed on the corrosion potential. Impedance diagrams are given in the Nyquist representation.

Surface analysis

The Scanning electron microscopy (SEM) micrographs of the samples were carried out by JEOL JSM 6460 LV SEM.

Results and Discussion

Chemical composition of the essential oil

Table 1 shows the chemical composition of the essential oil of Myrtle species. The oil is made up of two major compounds, 1,8-cineole and acetate myrtènyl. The chromatogram obtained is shown in **Figure 1**. The retention times and the relative percentages of the major components of the essential oil are shown in **Table** 1.

Gravimetric Study

The copper corrosion rate was determined gravimetrically after 1 hour of immersion in 2M HNO_3 without and with addition of inhibitor at various concentrations. The inhibitory effectiveness (IE%) of the compounds is calculated from the following relationship:

$$IE\% = \frac{W0 - W}{W0} \times 100 \qquad (1)$$

Table 1 Constituents of the essential oil Myrtle

Time (min)	Aire%	Made up
16,600	36.67	Acetate myrtènyl
21.101	13.22	α-pinene
21,300	48.81	1,8-cineole
24049	0.63	thujone (alpha)
33507	0.67	Isosafrole "cis"

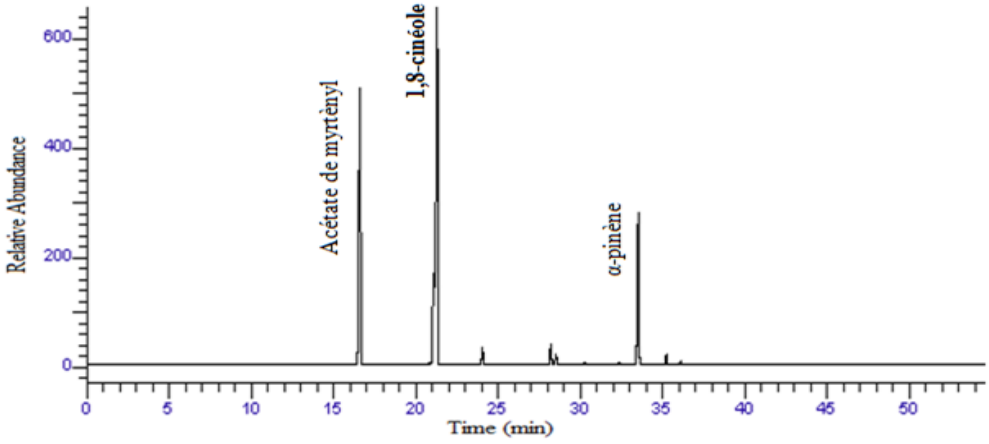

Figure 1 Chromatogram of the essential oil Myrtle.

Table 2 Corrosion rate and inhibitory efficiencies of copper in 2 M HNO_3 without and with addition of the essential oil of Myrtle at various concentrations at 25°C

	Inhibitor concentration (ppm)	W (mg/cm^2.h)	IE (%)
Blank	0	0.09375	—
Essential oil of Myrtle	1000	0.04762	49.20
	1200	0.03852	58.91
	1400	0.03157	66.32
	1600	0.02760	70.56
	1800	0.02549	72.81
	2000	0.02549	72.81

Where, W_0 and W are respectively the copper corrosion rates in medium 2M HNO_3 without and with addition of the test compound. The results of the study are summarized in **Table** 2.

Analyzing Table 2, we can see that increasing the inhibitor concentration is accompanied by a reduction in the corrosion rate. The inhibition efficiency reached 72.81% at 1800 ppm.

The corrosion rate of decrease (W) of the copper is probably due to the adsorption of the compounds of the essential oil of Myrtle to the metal surface.

Polarization curves

The copper polarization behavior in 2 M HNO_3 with and without the addition of this inhibitor is presented in **Figure 2**. The electrochemical parameters, corrosion current values (I_{corr}), the corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and the effectiveness of inhibition (% E) are given in **Table 3**.

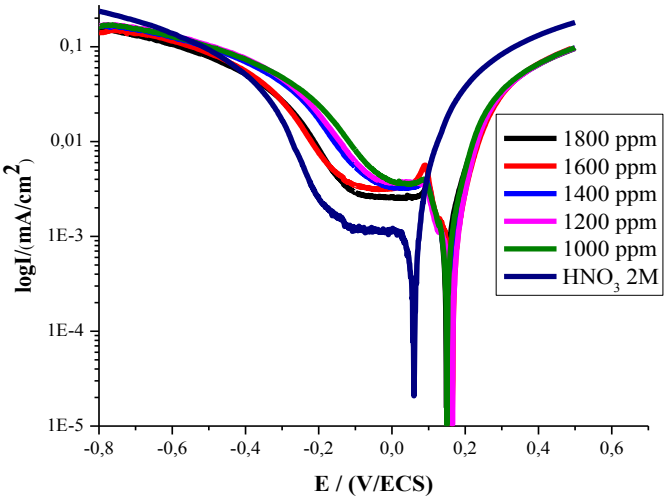

Figure 2 Copper polarization curves in 2M HNO_3 with and without the addition of essential oil Myrtle at various concentrations at 25 ° C

Table 3 Electrochemical parameters and inhibitory efficacy of the copper in 2M HNO_3 without and with addition of myrtle essential oil at different concentrations at 25°C

C_{INH}/(ppm)	E_{Corr}/(mV/ECS)	I_{Corr}/(mA/cm^2)	β_a/(mV)	β_c/(mV)	E%
Blank	65.2	2.1741	77.0	-349.5	—
1000	147.1	1.0303	73.1	-93.6	52.61
1200	163.2	0.7842	60.6	-120.8	63.92
1400	152.1	0.6456	51.8	-87.5	70.3
1600	148.7	0.5944	60.9	-82.9	72.66
1800	161.6	0.5695	50.2	-92.5	73.8
2000	163.3	0.5656	52.7	-134.4	73.98

The inhibitory effectiveness E% is defined by the following relationship:

$$E\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (2)$$

where I_{corr} and I'_{corr} respectively represent the corrosion's current densities determined by extrapolation of the straight Tafel to the corrosion potential with and without addition of inhibitor.

Examination of Figure 2 and Table 3 allows us to see that the addition of the test compound causes a shift in the corrosion potential with a tendency towards the anodic values due to the protective power vis-à-vis the inhibitor metal. This displacement is accompanied by a net decrease of current densities which is more accentuated when the concentration of the inhibitor increases to critical concentration at which there is an obtained a value of 0.5656 mA/cm^2 corresponding to an efficiency of 74%.

This decrease of the current bit can be explained by the inhibiting action of the inhibitor, due to the adsorption of chemical compounds present in the essential oil on the active sites of the surface of the electrode, therefore creating a barrier that slows the metallic copper dissolution in the anodic sites and blocking the release of the hydrogen by blocking the hydrogen reduction on the cathodic sites. The slight change in the Tafel slopes show that the reaction to the reduction of protons on the copper's surface is not modified by the addition of the inhibitor and it is achieved according to a pure activation mechanism.

The reduction in observed the corrosion speed by the gravimetric method may be explained by the action of anodic essential oil on the process of corrosion and therefore we can say that this natural inhibitor preferentially acts as anodic inhibitor. The values of the inhibitory effictiveess obtained by gravimetric and stationary electrochemical methods are in good agreement [15].

Monitoring of potential/time

Figure 3 shows the evolution in time of the copper in a nitric acid solution with 2 M and without an inhibitor.

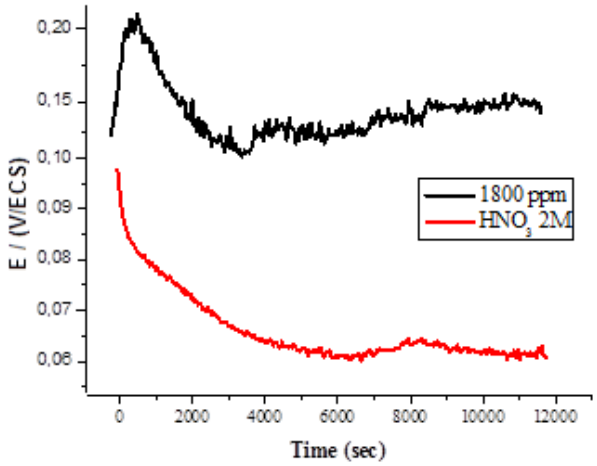

Figure 3 Monitoring the open circuit potential of copper immersed in 2M HNO_3 with and without inhibitor

The evolution of the potential to the test performed without inhibitor characterizes the corrosion of the sample with the formation of corrosion products. The stabilization of the free potential to a value of 64 mV is reached after 1 hour of immersion. With the addition of the inhibitor to 1800 ppm, we can observe an evolution of the potential namely an ennobling, after 10 minutes there is a drop in the potential which is stabilized after one hour of immersion in a value of 150 mV, which suggests corrosion primer. The film formed under these conditions would not be likely effectively protective of copper.

Electrochemical impedance spectroscopy measurement

The electrochemical impedance measurement is a particularly sui**table** technique for determining the action of the inhibitor mode; the evaluation of dielectric properties of the film formed and tracking their progress.
It also helps to explain the chemical or electrochemical process developing through the films formed. Thus, we have applied this technique to the study of the influence of the addition of the essential oil of Myrtle on the electrochemical behavior of the interface of the copper/2M HNO_3.

Figure 4 shows the electrochemical impedance diagram of copper obtained in 2M HNO_3 with and without addition of the inhibitor. The dielectric parameters of the metal/solution interface from this diagram are reported in **Table 4**.
The inhibitory effectiveness was determined by the following equation:

$$E\,\% = \frac{R_T' - R_T}{R_T'} \times 100 \qquad (3)$$

Where, R_T and R'_T are respectively the copper charge transfer resistance in 2M HNO_3 medium in the absence and presence of the inhibitor.

The charge transfer resistance values (R_T) were calculated based on the difference between impedance values at lower and higher frequencies.

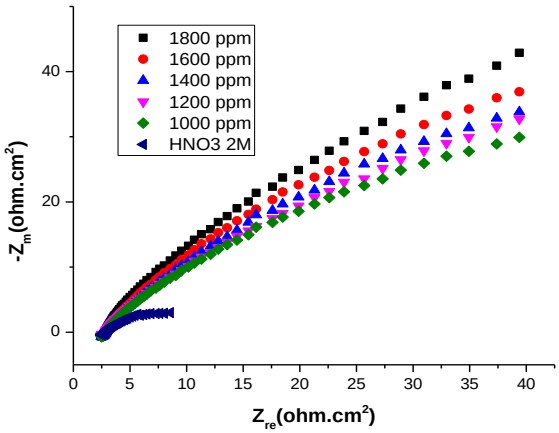

Figure 4 Electrochemical copper impedance diagrams with and without addition of the inhibitor 2M HNO_3 environment.

Table 4 Characteristics of copper electrochemical parameters of impedance diagram with and without addition of inhibitor 2M HNO_3, in the corrosion potential

Inhibitory concentration/ppm	R_T/ohm.cm^2	f_{max}/Hz	C_{dl}/µF/cm^2	E%
Blank	18.71	22.89	371.5	—
1000	37.56	31.62	134.0	50.18
1200	46.14	29.03	118.8	59.45
1400	57.13	24.24	114.9	67.25
1600	66.44	22.32	107.3	71.84
1800	69.60	21.57	106.0	73.12
2000	69.86	21.35	106.5	73.22

The ability of the double layer (C_{dl}) and the frequency (f_{max}) at which the imaginary component of the impedance is at maximum are shown in the following equation:

$$C_{dl} = \frac{1}{2\ \pi\ f_{max}\ R_T} \qquad (4)$$

The impedance spectra were as capacitive semicircles. The diameters of the semicircles increase with the increase of the inhibitor's concentration, indicating that the inhibition efficiency is a function of the inhibitor's concentration.

This type of diagram generally indicates that the corrosion of reaction is controlled by a charge transfer process on a solid electrode of heterogeneous and irregular surface.

The values of C_{dl} in the presence of the inhibitor are less than those of the blank value with a factor of 3, unlike the charge transfer resistance values which increase with the same factor when going from 18.71 to 69.60 with the addition 1800ppm of the inhibitor, confirming its adsorption on the metal surface forming an electronic doubled layer [16].

These results are in good agreement with those obtained by polarization where the essential oil of Myrtle proves to be a good inhibitor for copper in 2M HNO_3 acid with efficiency of 73%.

The equivalent circuit of said Randles used to study the impedance is given in **Figure 5**. The resistance R_e of the Randles circuit corresponds to the resistance of the finite conductivity of electrolyte. The interface charge phenomenon electrode/solution cause the appearance of a capacitive current (represented by the rated capacity C_{dl}). The resistance in transfer of the R_T charge is identified to the charge transfer resistance [17].

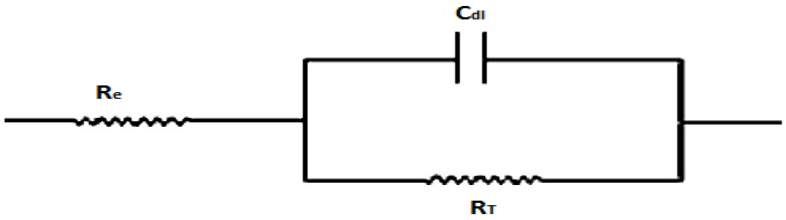

Figure 5 Equivalent circuit used to model the impedance diagrams made to corrosion potential

Temperature effect

Temperature is an important condition in the studies on the dissolution of the metal. The corrosion rates in acidic solutions, for example, increases exponentially with an increasing temperature due to the evolution of the hydrogen overvoltage decreasing [18].

Monitoring the open circuit potential allows to keep track of the changes to the interface between the material and the environment.

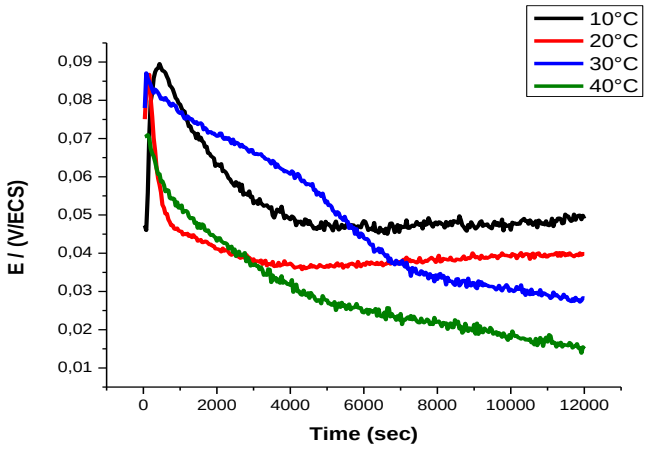

Figure 6 Monitoring the open circuit potential of copper immersed in 2M HNO_3 solution at different temperatures

Figure 6 shows the evolution of the free potential of copper in nitric acid 2M for 12 000 seconds respectively at each test temperature. No matter what the temperature is, the variation of the potential versus time is a characteristic of a corrosion mechanism with formation of corrosion products. The potential decreases during the first few minutes and stabilizes at 66 minutes for the curves at 10 and 20°C and stabilizes at 120 minutes to the curves 30 and 40°C. This observed difference is due to the change attributed to a more rapid dissolution of copper for high temperatures. This result is confirmed by the polarization curves.

The evolution of the free potential versus time recorded in 2M HNO_3 with 1800 ppm of the inhibitor at different temperatures shows the existence of two distinct temperature ranges, where the behavior of copper looks different against corrosion (**Figure 7**).

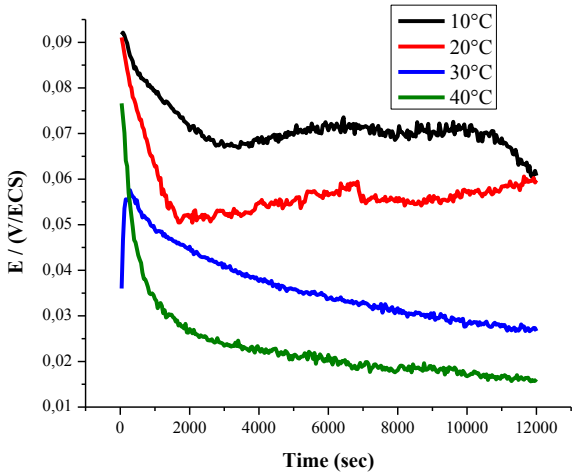

Figure 7 Followed by the open circuit potential of copper immersed in the solution with 2M HNO_3 1800 ppm of essential oil of Myrtle at different temperatures

At temperatures of 10-20°C, the potential is stabilized after about 35 minutes of immersion while it stabilizes after 1 hour 30 minutes at temperatures 30°C- 40°C. This behavior may characterize an early inhibition. The film formed would protect copper lasting but not as effectively at lower temperatures.

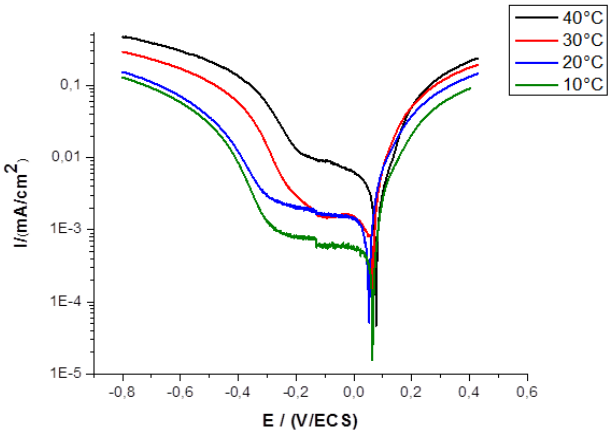

Figure 8 Effect of temperature on the cathode and anode reactions of copper in 2M HNO_3

Different amperage values I_{corr} were obtained by the extrapolation of Tafel straight experiments conducted at 283, 293, 303, and 313 K. The polarization curves shown in **Figures 8** and **9** illustrate respectively the copper in a 2M HNO_3 solution with and without inhibitor, in the temperature range (273-313 K). The different numerical values of

the variation of the corrosion's current density (I_{corr}), the corrosion potential (E_{corr}), cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) to 1800 ppm inhibitor are studied at different temperatures given in **Table 5**.

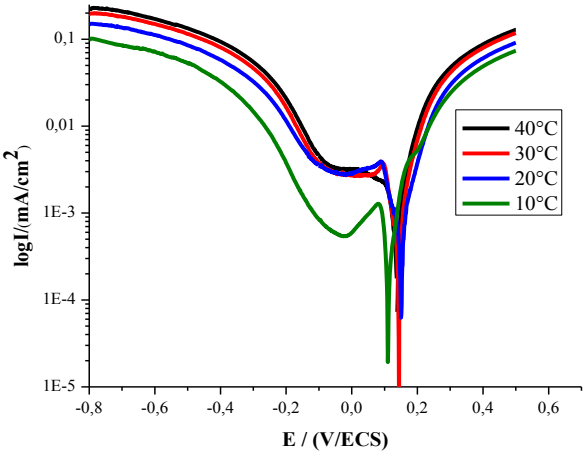

Figure 9 Effect of temperature on the cathode and anode reactions of copper in 2M HNO_3 with 1800 ppm essential oil of myrtle

Table 5 Electrochemical parameters of copper in 2M HNO_3 without and with 1800 ppm of inhibitor, at different temperatures

Inhibitor	Temperature/(K)	E_{Corr}/(mV/ECS)	I_{Corr}/(mA/cm^2)	β_a/(mV)	β_c/(mV)	IE%
Blank	283	75.8	1.5387	66.1	-77.3	—
	293	64.1	1.9411	126.4	-84.5	—
	303	50.3	2.9902	123.1	-91.6	—
	313	66.4	3.6507	98.6	-65.8	—
1800 ppm of oil	283	109.1	0.1833	37.2	-22.9	88.08
	293	148.8	0.4837	69.9	-130.6	75.08
	303	141.9	0.9416	52.4	-64.1	68.51
	313	137.0	1.3792	55.8	-95.2	62.22

In the absence and presence of the inhibitor, the I_{corr} value increases as the temperature increases. It is also evident that the essential oil myrtle has inhibitory properties at all temperatures studied and values of the effectiveness of inhibition decreases with increasing temperature.

This means that the inhibitor is adsorbed on the substrate by electrostatic nature of bonds (weak bonds). This type of temperature-sensitive links cannot fight effectively against corrosion with an increasing temperature [19].
In the case of the acid corrosion, many authors [20], use the Arrhenius equation to highlight the effect of temperature on the rate of corrosion and therefore consider that the logarithm of the speed Corrosion is a linear function of T^{-1}. We can calculate the activation energies from the following relationships:

$$I_{Corr} = K \exp(-E_a/R_T) \quad (5)$$
$$I'_{corr} = K' \exp(-E'_a/R_T) \quad (6)$$

where k and k' are constants (pre-exponential parameter Arrhenius), and E_a and E'_a activation energies, respectively, in the absence and presence of the inhibitor.

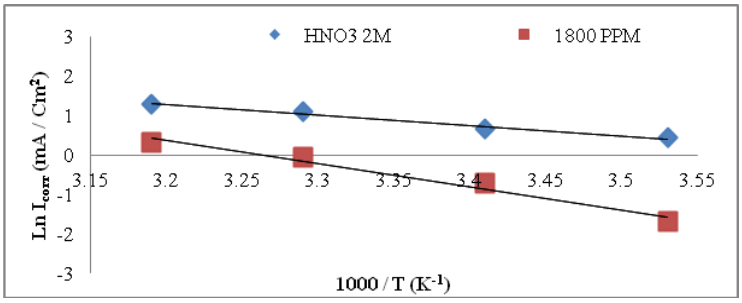

Figure 10 Arrhenius diagram of the dissolution of copper in 2M HNO_3 at different temperatures with and without inhibitor

Table 6 Copper dissolution activation energy in 2M HNO_3 alone and in the presence of the inhibitor

Sample	Ea / (kJ / mol)
Blank	22.08
Essential oil of Myrtle	49.29

Some conclusions on the action mechanism of the inhibitors may be obtained by comparing measured Ea to both the presence and absence of the corrosion inhibitor. **Figure 10** shows the Arrhenius plot coordinates of the copper corrosion rate in 2M HNO_3 in the absence and presence of the essential oil of Myrtle to 1800 ppm.

The variation of the logarithm of the corrosion current as a function of T^{-1} gives lines showing that the Arrhenius law is satisfied. The values of the activation energy obtained from these lines are given in **Table 6**.

Given the results of Table 6, it is noted that the presence of the inhibitor the activation energy increases, so that the inhibitory efficiency decreases as the temperature increases. This behavior demonstrates that the inhibitor adsorbs on the metal surface by electrostatic nature of bonds (weak bonds).

The values of the activation energy obtained from straight Arrhenius is 22 KJ/mol^{-1} in the absence of inhibitor, this value is in agreement with the literature [21], and at a concentration of 1800 ppm of the inhibitor, i.e., of when the recovery rate is at maximum, the value of the activation energy in the presence of this oil is 49 kJ/mol^{-1}. This confirms the physical adsorption of the inhibitor by forming a surface film which does not allow fighting effectively against corrosion with increasing temperature.

The kinetic parameters, the enthalpy and entropy of the corrosion process are also evaluated from the study of the temperature effect. An alternative formulation of the Arrhenius equation is [22]:

$$I_{corr} = \frac{R\,T}{N\,h} \times \exp\left(\frac{\Delta S^*}{R}\right) \times \exp\left(-\frac{\Delta H^*}{R\,T}\right) \qquad (7)$$

Where, *h* is Planck's constant, N is the number of Avagadro, ΔS* is the entropy of activation and the ΔH*is the activation enthalpy. **Figure 11** shows plots of Ln (I_{corr}/T) versus 1/T. The straight lines are obtained with a slope - ΔH*/R and an intercept (Ln R/Nh + ΔS*/R), from which the values of ΔS* and ΔH* can be calculated, these values are given in **Table 7**.

The positive sign of ΔH* reflects an endothermic adsorption process [23]. Negative values of entropy ΔS*, reflects an increase of disorder that occurs during the formation of the metal complex/adsorbed species [24].
Moreover

$$\Delta G^* = - R \times T \times \mathrm{Ln}\,(55.5 \times K) \qquad (8)$$

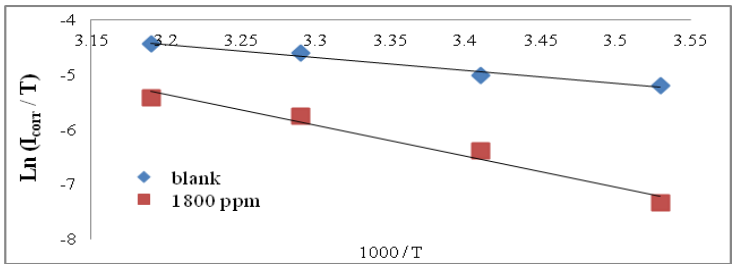

Figure 11 Relations between Ln (I_{corr} / T) and 1000 / T at different temperatures

Table 7 The values of the activation parameters ΔS* and ΔH* of copper in 2M HNO_3 in the absence and in the presence of 1800 ppm the essential oil myrtle at T = 293K

Inhibitor	ΔH* (KJ/mol)	ΔS* (J/mol.K)
Blank	19.64	-171.75
inhibitor	46.85	-251.29

$$K = \frac{\Theta}{C\times(1-\Theta)} \qquad (9)$$

where R is the universal gas constant, 55.5 is the water concentration in mol/L, Θis the degree of coverage of the metal surface, and C is the concentration of inhibitor in ppm.

The negative value ΔG* = -20.65 kJ/mol at 25°C indicates the spontaneity of the adsorption process, and the stability of the adsorbed layer on the metal surface due to electrostatic interactions between the charged molecules and the metal [25].

Surface analysis

SEM micrographs of the surfaces of the copper corroded samples after the potentiodynamic polarization in 2M HNO_3 solution (a) and after polarization in a 2M HNO_3 solution with 1800 ppm of the essential oil myrtle (b) are shown in **Figure 12**.

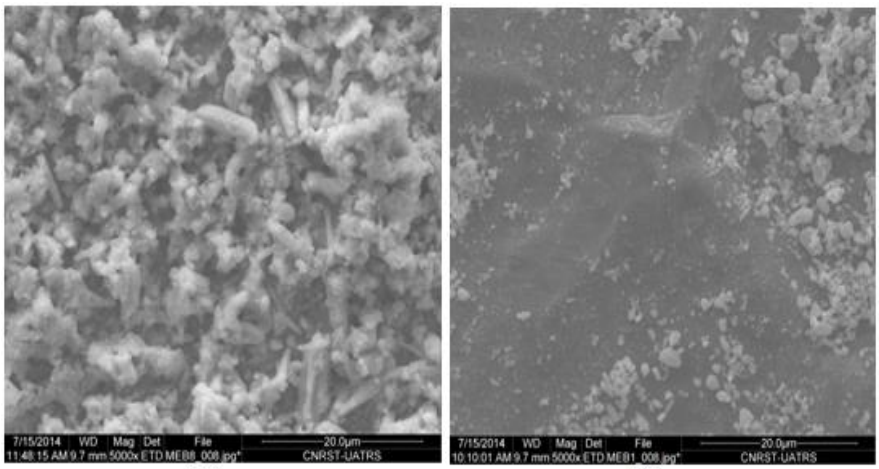

Figure 12 SEM micrographs of the samples of the copper surface after the electrochemical tests (polarization measurements) in a solution of 2M HNO_3: (a) without oil Myrtle; (b) containing 1800 ppm of oil Myrtle.

Figure 12a shows that the treatment of the copper sample using the potentiodynamic polarization in 2M HNO_3 solution leads to the formation of crystallographic forms (rough surface) of the uniform corrosion characteristics indicating that the copper in the solution is strongly corroded [26]. By comparing SEM images at the same magnifications (Fig. 12a and b), it is clear that the addition of 1800 ppm of the essential oil of myrtle shows an improvement of the morphology of the copper surface represented by a smooth surface protected by oil. Therefore, there is good agreement between the results of SEM, weight loss measurements and potentiodynamic measurements. We note that the inhibitory action of the essential oil of myrtle may also be caused by the synergistic interaction of the active molecules of this oil.

Conclusion

It appears from this study that:

1. The essential oil of myrtle is an effective inhibitor of the corrosion of copper in a HNO3 solution 2 M. The inhibitory effectiveness increases with the concentration to achieve 73% to 1800 ppm.
2. The results of the Polarization studies suggest that the inhibitor acts mainly by an anodic process.
3. The results of the electrochemical impedance spectroscopy indicate that adsorption of the inhibitor on the surface of the copper increases the transfer resistance and reduces the capacity of the doubled layer.
4. The adsorption process is a stable and endothermic process.
5. The inhibitors effectiveness values determined by electrochemical polarization, electrochemical impedance spectroscopy and by gravimetric methods are in good agreement.

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