Research Article

Corrosion Inhibition of Copper in 2M HNO$_3$ using the Essential Oil *Eugenia caryophyllus*

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Abstract

The inhibition of copper corrosion by the essential oil of species *Eugenia caryophyllus* has been studied in a 2 M solution of nitric acid using the method of weight loss, the potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and measuring the open circuit potential. An efficacy of 70% inhibition was obtained with the addition of 1600 ppm of oil. The potentiodynamic curves show that the decrease of corrosion of copper in the presence of the essential oil of *Eugenia caryophyllus* in 2M nitric acid solution is a cathode mainly by process. The results by gravimetric (weight loss), potentiodynamic polarization and impedance measurements showed similar values of the effectiveness of inhibition.

Keywords: copper corrosion inhibition, the essential oil of *Eugenia caryophyllus*, adsorption.

The adsorption of the essential oil of *Eugenia caryophyllus* on the copper surface in a solution of 2 M nitric acid follows the Langmuir isotherm model.
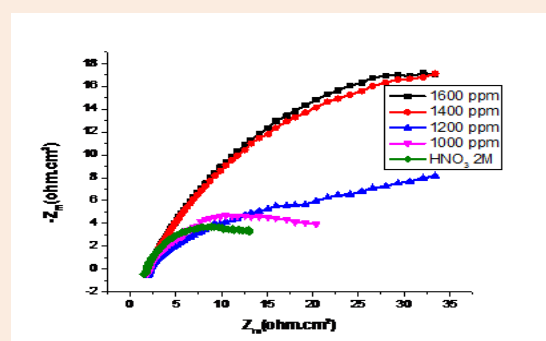
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Introduction

Excellent thermal conductivity, good corrosion resistance and mechanical workability are of physical properties of copper that explain the major applications of copper and its alloys in different industries. However, most industrial processes lead to corrosion problems. Copper in general corrode when exposed to the ammonia, oxygen, or liquids with high sulfur content. Another source of copper corrosion is the presence of anions in the environment, such as chlorides, sulfates and bicarbonates. In industries, hydrochloric acid and nitric acid is widely used for acid pickling, acid cleaning and removing rust and decaling acids [1]. Therefore, the corrosion process controls under the influence of acidic conditions are important subjects worthy of intensive research.

One of the most important methods and practices of the protection against corrosion of metals is the use organic inhibitors which protect the metal surface from the corrosive environment [1,2]. Generally the organic compounds containing heteroatoms such as oxygen, nitrogen or sulfur, behaves quite well as a corrosion inhibitor in an acid medium [3]. The strength of the coordinate bond heteroatoms (O <N <O <P) approaches its effectiveness as corrosion inhibitors.

Due to environmental requirements currently imposed environmental corrosion inhibitors, there is a growing interest in the use of natural products such as extracts of leaves, seeds or bark extracts. Some Items reported the use of natural products in the development of green corrosion inhibitors as effective for different metals in various environments [4-22]. Essential oils have a non-toxic category made of biodegradable organic compounds. These oils

are known and used for over 7000 years. From nature and created by it, they consist exclusively of odorous volatile terpene molecules in producing organs of plants and aromatic trees.

The aim of this work is the study of the corrosion inhibition of copper in 2M HNO_3 by the essential oil of *Eugenia caryophyllus* not toxic nail by electrochemical and gravimetric measurements.

Experimental

Extraction of the essential oil of Eugenia caryophyllus (CEO)

The essential oil of this species belonging to the family Myrtaceae is obtained by steam distillation of water using a distiller Clevenger kind for 3h. The yield of essential oil of *Eugenia* is 15 %. 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 to mass spectrometry. The other part was used for testing anti corrosion activity. The oil obtained after extraction was recovered and stored in a dark bottle and stored at 4 °C before use.

Preparation of the solution

The 2 M HNO_3 solution was prepared by dilution of the nitric acid of analytical grade 67% 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 conducted by maintaining the desired temperature of the electrolyte with a thermostat FRIGITHERM mark. The electrolyte volume was 30 mL. The samples are rectangular form surface 9.6 cm^2. Prior to measurements, they undergo a mechanical polishing with abrasive paper of up to 1200 increasing size, followed by degreasing with acetone, followed by washing with distilled water and drying in air. Each value of the gravimetric test is the average of at least three tests.

Measures electrochemical

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

The current-potential curves are obtained by potentiodynamic method; the potential applied to the sample varies continuously with a scanning rate of 30 mV / min. We chose a relatively low rate of scanning to be quasi-steady. Before curve plot, the working electrode is maintained at a potential of -800 mV for 15 minutes.

The measures electrochemical impedance spectroscopy (EIS) was performed with the same electrochemical system. The frequencies between 100 Hz and 10 kHz were superposed on the corrosion potential. The diagrams given in the impedances are Nyquist representation.

Results and Discussion

Analysis of the essential oil of Eugenia caryophyllus

Table 1 shows the chemical composition of the essential oil of *Eugenia caryophyllus*. The oil is mainly constituted by eugenol (2-methoxy-4-(2-propenyl) phenol) (82.94%) and eugenyl acetate (4-allyl-2-methoxy-phenyl acetate)

(9.32%).The chromatogram obtained is shown in Figure 1. The retention time and the relative proportion of the constituents of the essential oil are shown in Table 1.
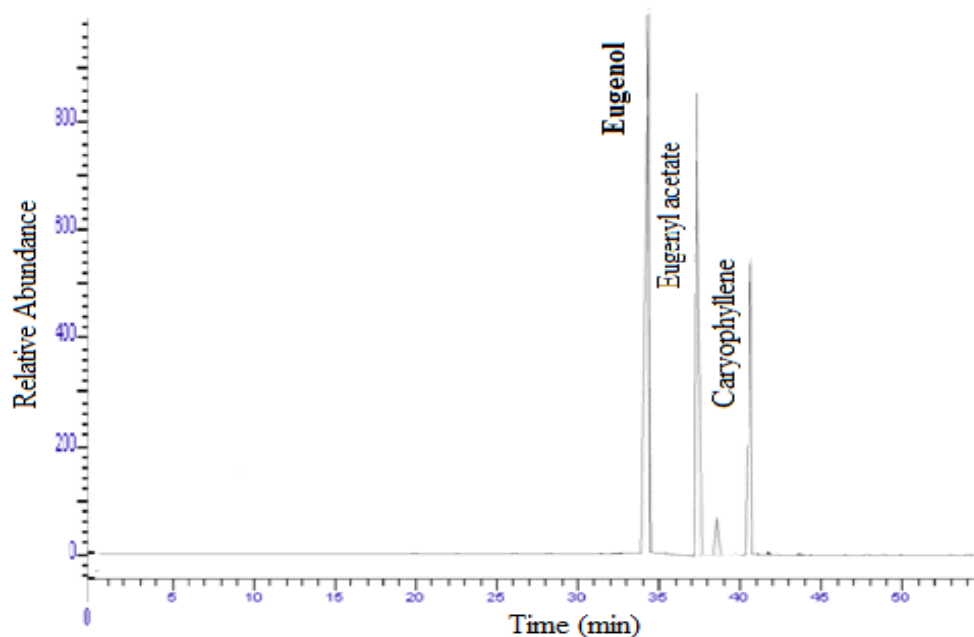

Figure 1 Chromatogram of the essential oil of *Eugenia caryophyllus.*

Table 1 Constituents of the essential oil of *Eugenia caryophyllus*

Time (min)	Area%	Compound
34495	**82.94**	**Eugenol**
37176	9.32	Eugenyl acetate
38244	0.58	Farnesene "cross-beta"
40207	7.17	Caryophyllene

gravimetric Study

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

$$EI\% = \frac{w_0 - w}{w_0} \times 100$$

(1)

Where, W and W0, respectively, the corrosion rates of copper in 2 M HNO_3 without and with addition of test compound. The results of the study are summarized in Table 2.

Table 2 Corrosion rate and inhibitory efficiencies of copper in 2 M HNO$_3$ with and without addition of the essential oil of *Eugenia caryophyllus* at different concentrations at 25 °C

	Inhibitor Concentration (ppm)	W (mg/cm^2.h)	EI (%)
Blanc	0	0.09375	
Essential oil of *Eugenia caryophyllus*	1000	0.0757	19.25
	1200	0.06318	32.61
	1400	0.0428	54.35
	1600	0.03207	66.79
	1800	0.03207	66.79

Analysis of Table 2, we can see that increasing the inhibitor concentration is accompanied by a decrease in the corrosion rate. The inhibition efficiency reached 66.79% at 1600 ppm.

This reduction in corrosion rate (W) of the copper is probably due to the adsorption of these compounds to the metal surface.

Polarization curves

The polarization behavior of copper in 2 M HNO$_3$ with and without addition of this inhibitor is presented in Figure 2. Electrochemical parameters, values of corrosion current (Icorr), the corrosion potential (E$_{corr}$), cathodic Tafel slope (βc), anodic Tafel slope (βa) and efficacy of inhibition (% E) are given in Table 3.

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

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

Where I'corr Icorr and respectively represent corrosion current densities determined by extrapolation of the straight Tafel corrosion potential with and without addition of inhibitor.
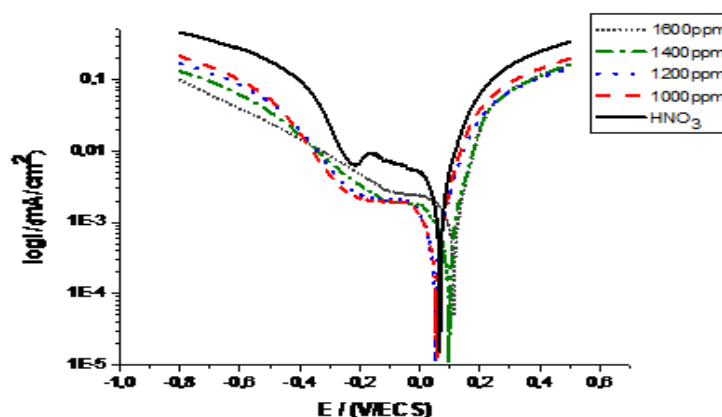

Figure 2 Polarization curves of copper in 2M HNO$_3$ without and with addition of the essential oil of *Eugenia caryophyllus* at various concentrations at 25 ° C.

Table 3 Electrochemical parameters and inhibition efficiency of copper in 2M HNO_3 with and without addition of the essential oil of *Eugenia caryophyllus* at different concentrations at 25 °C

C_{INH} / (ppm)	E_{Corr} / (mV / SCE)	I_{Corr} / (mA / Cm^2)	βa / (mV)	βc / (mV)	E%
Blank	65.2	2.1741	77.0	-349.5	---
1000	54.9	1.6957	55.8	-119.9	22.00
1200	52.8	1.3816	58.3	-101.5	36.45
1400	98.0	0.9292	45.4	-83.7	57.26
1600	113.5	0.6494	44.2	-72.6	70.13
1800	112.8	0.6391	43.1	-68.1	70.60

Examination of Figure 2 and Table 3 allow us to conclude that the addition of the test compound causes a slight shift of the corrosion potential but with a trend toward cathodic values. This displacement is accompanied by a net decrease of current densities which is more marked when the concentration of inhibitor increases until a critical concentration at which value 0.6494 mA / Cm^2 is obtained corresponding to an effective 70%.

This decrease of the current bit to be explained by the inhibiting action of the inhibitor, due to the adsorption of chemical compounds in the essential oil on the surface of active electrode sites, creating a barrier that slows the dissolution of metallic copper in the anodic sites and blocking the release of hydrogen in the reduction of blocking hydrogen at cathodic sites.

The addition of the inhibitor was varied slightly values Tafel slopes. This result suggests that the reaction mechanism is not substantially affected by the addition of the inhibitor.

In the light of these results we noted the mixed nature of the inhibitor used with predominant cathodic effectiveness [23].

Followed by open circuit potential

Figure 3 shows the change of corrosion potential versus time of the copper in a 2 M nitric acid solution with and without inhibitor.
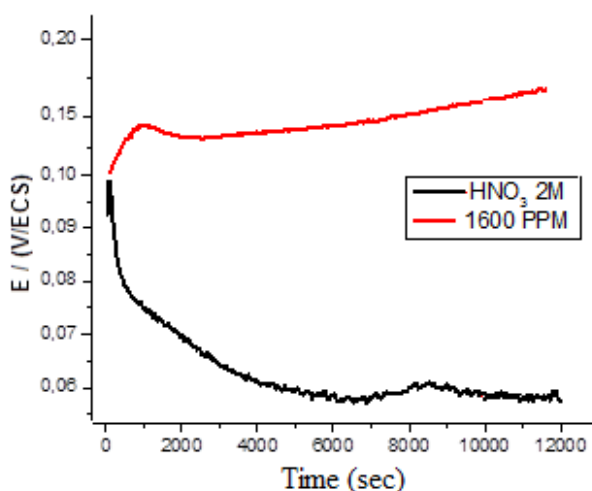
Figure 3 Followed by open circuit potential of copper immersed in 2M HNO_3 with and without inhibitor.

The evolution of the abundant potential for the test performed without inhibitor characterizes the corrosion of the sample with the formation of corrosion products. Stabilization of free potential value 64 mV is reached after 30 minutes of immersion. With the addition of the inhibitor to 1600 ppm, there is a potential of ennobling. The evolution of the free potential, in this case, indicates the formation of a protective layer.

Measurement of electrochemical impedance spectroscopy

The electrochemical impedance measurement technique is particularly suitable for determining the mode of inhibitor action, evaluation of dielectric properties of the film formed and follows their evolution.

It also helps to explain the chemical or electrochemical process developing through the films formed. Thus, we applied this technique to study the influence of the addition of the essential oil of *Eugenia caryophyllus* on the electrochemical behavior of the interface of copper / 2M HNO_3.

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

The inhibitory effectiveness was determined by the equation 3:

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

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

The double layer capacity (C_{dl}) and the frequency (fmax) at which the imaginary component of the impedance is maximum are shown Equation 4:

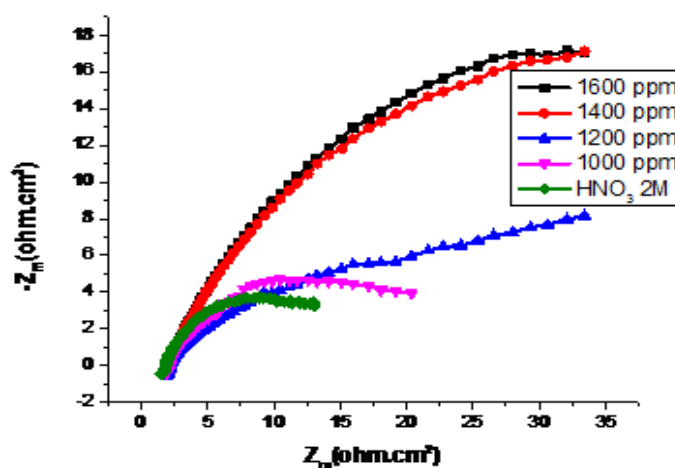$$C_{dl} = \frac{1}{2\pi\, fmax\, RT} \qquad (4)$$

Figure 4 Diagram of electrochemical impedance copper with and without addition of inhibitor in 2M HNO_3.

The impedance spectra are simple form semicircles, and the semicircles diameter increases with increasing inhibitor concentration. The presence of a single half-circle indicates that the charge transfer occurs at the electrode / solution interface, and the process of charge transfer reaction of the copper corrosion inhibitor in the presence of the mechanism does not change its dissolution.

Table 4 Parameters electrochemical characteristics of impedance diagram of copper with and without addition of inhibitors 2M HNO_3, in the corrosion potential

Inhibitor concentration / ppm	R_T / ohm.cm^2	fm / Hz	Cdl / µF/cm^2	E%
Blank	18.71	22.89	371.5	-----
1000	23.67	26.06	258.0	20.95
1200	31.10	20.33	251.7	39.84
1400	41.55	16.07	238.3	54.97
1600	63.44	14.46	173.5	70.50
1800	63.55	14.66	170.8	70.56

Values increase with increase of the concentration of essential oil of *Eugenia caryophyllus*, whereas C_{dl} values decrease. Higher values may suggest the formation of a protective layer on the surface of the electrode [24]
The C_{dl} values are considered below those of the blank value, confirming the adsorption of inhibitor onto the metal surface forming an electronic double layer [24].

These results are in good agreement with those obtained by polarization where the oil essential *Eugenia caryophyllus* proves to be a good inhibitor for copper in 2M HNO_3 acid with efficiency of 70%.
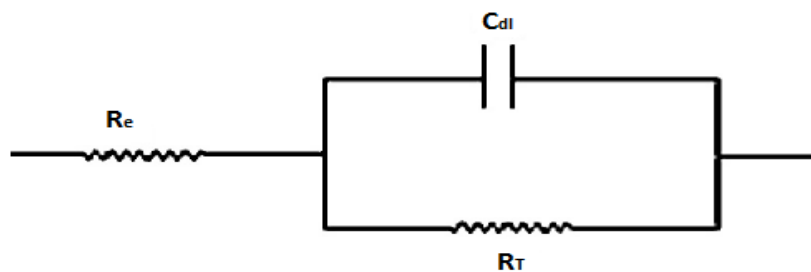

Figure 5 Equivalent circuit used for modeling the impedance diagrams made to corrosion potential.

The equivalent circuit of said Randles used to study the impedance is given in Figure 5. Re is the resistance of the Randles circuit Corresponds to the resistance of the electrolyte finite conductivity. The charge phenomenon of the electrode / solution interface causes the appearance of a capacitive current (represented by the rated capacity C_{dl}). The charge transfer resistance RT is identified in charge transfer resistance [25].

Effect of temperature

The temperature is an important condition in the studies on the dissolution of the metal. The rate of corrosion in acidic solutions, for example, increases exponentially with increasing temperature due to the evolution of the hydrogen overvoltage decreasing [26].

Monitoring the open circuit potential function of temperature

Monitoring the open circuit potential saves the changes to the interface between the material and the environment. Figure 6 shows the evolution of the free potential of copper in 2M nitric acid for 200 seconds, respectively for each test temperature. Whatever the temperature, the change in potential with time is characteristic of a mechanism of corrosion with formation of corrosion products. The potential decreases during the first few minutes and stabilizes at 66 minutes for the curves 10 and 20 °C and 120 minutes to stabilize for curves 30 and 40 °C. This observed difference is due to the evolution that is attributed to a more rapid dissolution of copper for high temperatures. This result is confirmed by the polarization curves.
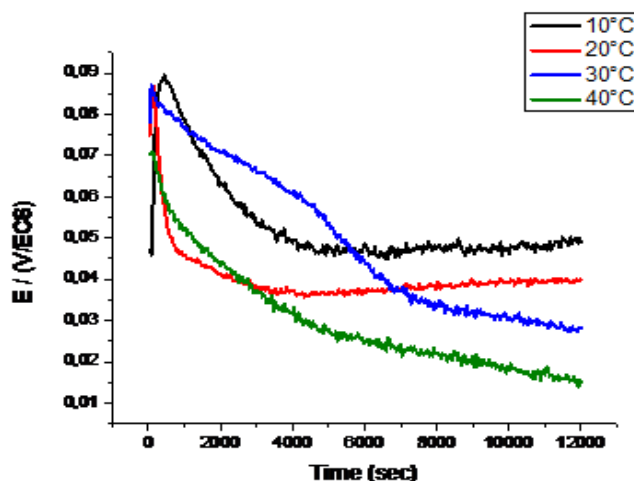

Figure 6 Followed by open circuit potential of copper immersed in 2M HNO_3 solution at different temperatures.
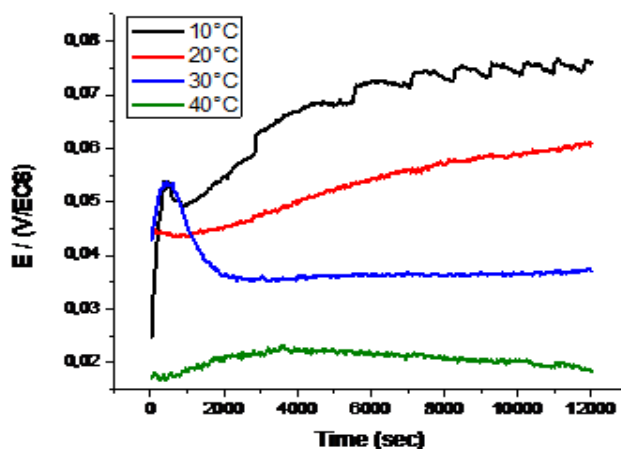

Figure 7 Followed by open circuit potential of copper immersed in 2M HNO_3 solution with 1600 ppm of essential oil of *Eugenia caryophyllus* at different temperatures.

The evolution of free potential function of time recorded in 2M HNO_3 with 1600 ppm inhibitor at different temperatures shows the existence of two distinct fields of temperature, where the behavior of copper looks different vis-à-vis the corrosion (figure 7).

In the field of temperatures 10-20°C, the potential increases with time. This curve is characteristic of the formation of a film on the surface of the active electrode. The continuous increase in the potential of the open time to spontaneous adsorption of the inhibitor molecules to the metal surface circuit.

At temperatures of 30-40 °C, the potential is stabilized after about 30 minutes of immersion. This behavior may characterize an early inhibition. The film formed would protect copper lasting but not efficiently to lower temperatures.

Effect of temperature on the polarization curves

Different current intensity Icorr values were obtained by extrapolating the straight Tafel experiments conducted at 283, 293, 303, and 313 K. The polarization curves shown in Figures 8 and 9 illustrate the copper in 2M HNO3 solution respectively with and without inhibitor, in the temperature range (273-313 K). The various numerical values of the variation of the corrosion current density (Icorr), the corrosion potential (Ecorr), cathodic Tafel slope (βc), and anodic Tafel slope (βa) to 1600 ppm inhibitor are studied at different temperatures given in **Table 5**.
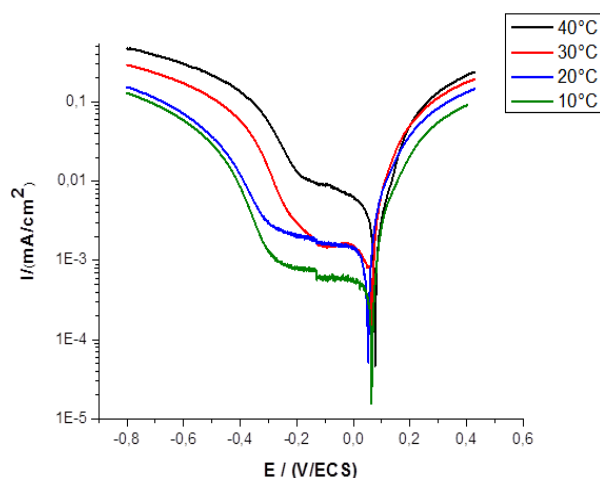

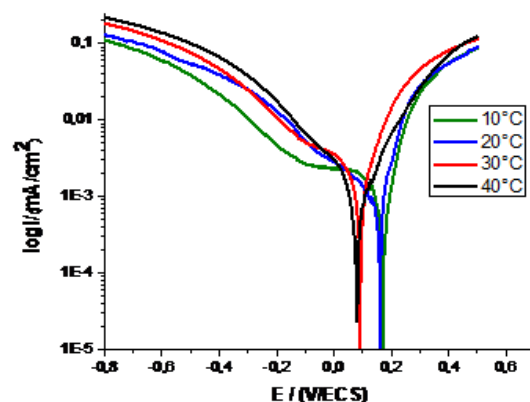**Figure 8** Effect of temperature on the cathode and anode reactions copper in 2M HNO_3

Figure 9 Effect of temperature on the cathodic and anodic reactions of copper in 2M HNO_3 with 1600 ppm of essential oil of *Eugenia caryophyllus*.

Table 5 Electrochemical parameters of copper in 2 M HNO$_3$ without and with 1600 ppm of inhibitor, at different temperatures

Inhibitor	Temperature / (K)	E$_{Corr}$ / (mV / SCE)	I$_{Corr}$ / (mA / cm^2)	βa / (mV)	-Bc / (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	---
1600 ppm of the essential oil of *Eugenia caryophyllus*	283	168.0	0.6216	48.6	59.8	79.21
	293	157.3	0.3329	62.9	180.4	78.36
	303	117.5	0.9712	79.5	134.4	67.52
	313	87.2	1.3719	91.7	148.4	62.42

In the absence and presence of inhibitor, the Icorr value increases with increasing temperature. It is also evident that the essential oil of *Eugenia caryophyllus* has inhibitory properties at all temperatures studied, and the values of the effectiveness of inhibition decreases with increasing temperature.

This means that the inhibitor is adsorbed on the substrate by electrostatic bonds Nature (weak bonds). This type of temperature-sensitive links cannot fight effectively against corrosion when the temperature increases [27].
In the case of the acid corrosion, many authors [28] use of the Arrhenius equation to account for the effect of temperature (T) on the rate of corrosion and therefore believe that the logarithm of the speed Corrosion is a linear function of T 1. We can calculate the activation energy from the following equations:

$$I_{Corr} = K \exp(-Ea / RT) \tag{5}$$
$$I'_{corr} K = \exp(-E'a / RT) \tag{6}$$

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

Some conclusions on the mechanism of action of the inhibitors may be obtained by comparing measured Ea to both the presence and absence of the corrosion inhibitor. The Figure 10 shows the Arrhenius plot of coordinates in the corrosion rate of copper in 2M HNO$_3$ in the absence and presence of the essential oil of *Eugenia caryophyllus* to 1600 ppm.
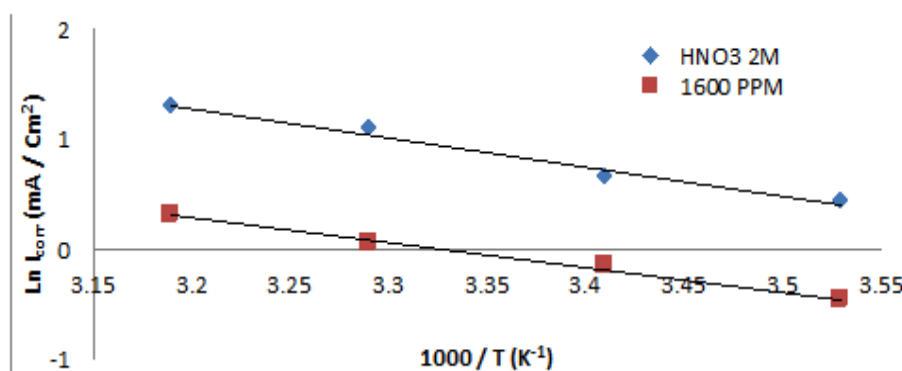
Figure 10 Arrhenius diagram of the dissolution of copper in 2M HNO$_3$ at different temperatures with and without inhibitor.

The variation of the logarithm of the corrosion current as a function of T^{-1} gives straight indicating that the Arrhenius law is enforced. The values of the activations obtained from these straight energies are given in Table 6.

Table 6 Activation energy of copper dissolution in 2M HNO_3 alone and in the presence of the inhibitor

Sample	Ea / (kJ / mol)
Blank	22.08
Essential oil of *Eugenia caryophyllus*	18.82

From the results of **Table 6**, it is noted that the presence of inhibitor decreases the activation energy, as the inhibitory efficiency which decreases with increasing temperature. This behavior demonstrates the phenomenon of chemisorption of the inhibitor to the metal surface.

This phenomenon can also be explained by the fact that the process of corrosion of copper in the presence of the inhibitor does not only depend on the reaction which takes place at the surface of bare metal, but also the release of Cu^{2+} ions through the layer of adsorbed inhibitor [29].

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 [30], and at a concentration of 1600 ppm of inhibitor, i.e. when the rate of recovery is maximum; the value of the activation energy in the presence of this oil is 18 kJ mol^{-1}. This confirms the chemical adsorption of the inhibitor by the effective formation of a surface film.

The kinetic parameters, the enthalpy and entropy of the corrosion process are also estimated from the study of the effect of temperature. An alternative formulation of the Arrhenius equation is [31]:

$$I_{corr} = \frac{RT}{Nh} \times \exp\left(\frac{\Delta S^*}{R}\right) \times \exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (7)$$

Where, h is Planck's constant, N is the Avagadro number, ΔS^* is the entropy of activation and the ΔH^* is activation enthalpy. Figure 11 shows plots of Ln (I_{corr} / T) versus 1 / T. The straight lines are obtained with a slope of $-\Delta H^*$ / 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.
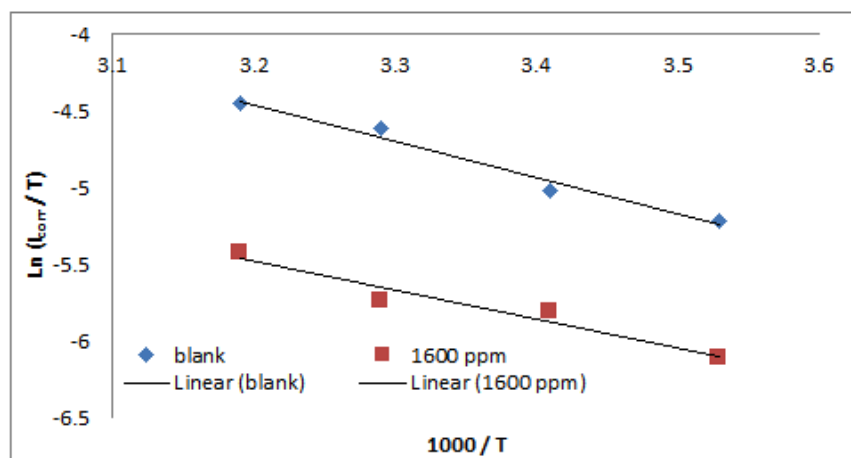

Figure 11 Relationship between Ln (I_{corr} / T) and 1000 / T at different temperatures

Table 7 The values of the activation parameters, ΔH^* and ΔS^* of copper in 2M HNO_3 in the absence and presence of 1600 ppm of essential oil of *Eugenia caryophyllus* at T = 293K

Inhibitor	ΔH^* (KJ / mol)	ΔS^* (J / mol.K)
Blank	19.64	-171.75
inhibitor	15.53	-193.44

The positive sign of ΔH^* reflects an endothermic process of adsorption, which is assigned to the chemisorption. [32] Negative values of entropy ΔS^*, reflects an increase of disorder that occurs during the formation of metal / adsorbed [33] species complex.
More

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

$$K = \Theta / C \times (1 - \Theta) \qquad (9)$$

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

The negative value of $\Delta G^* = -58.45$ kJ / mol at 25 °C indicates the spontaneous adsorption process, and the stability of the adsorbed layer on the metal surface involves a charge transfer between organic molecules and the surface a metal by chemisorption phenomenon [34].

Adsorption isotherm

The adsorption behavior provides information on the interaction between the adsorbed molecules and their interactions with the surface of the electrode [35].

The adsorption Temkin, Frumkin isotherm and Langmuir were used to represent the adsorption of the essential oil of *Eugenia caryophyllus* on the copper surface. The correlation coefficient, R^2, was used to choose the isotherm that best matches the experimental data. The recovery rate (θ) at different concentrations for the inhibitor tested in 2M HNO_3 was assessed from measurements of weight loss.
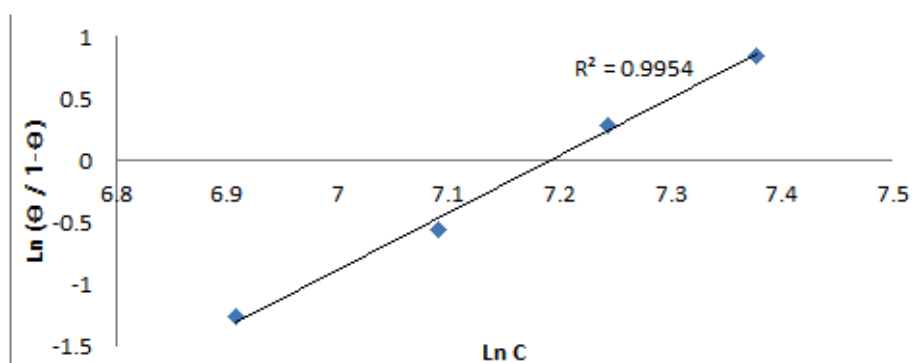

Figure 12 Model Langmuir isotherm for the adsorption of the inhibitor on the surface of copper in 2 M HNO_3 at 25 °C.

The curve representing ln (θ / θ-1) as a function of ln [C], where C is the concentration of inhibitor, is a straight line (Figure 12) indicating that the adsorption of the inhibitor on the surface of the copper plate is according to the Langmuir model:

$$Ln (θ / 1-θ) = K \ln [C]$$

The strong correlation ($R^2 = 0.9954$) for a portion of the field of isothermal Langmuir adsorption inhibitor confirms the validity of this approach.

Conclusions

The following conclusions can be drawn from this study:

- The essential oil of *Eugenia caryophyllus* is an effective inhibitor of the corrosion of copper in a solution of HNO_3 2 M. The inhibitory efficiency increases with the concentration to 70% at 1600 ppm.
- The results of the studies suggest that the inhibitor polarization mainly by a cathodic process.
- Results from electrochemical impedance spectroscopy indicate that adsorption of the inhibitor on the surface of the copper increases the strength and lowers the transfer capacity of the double-layer.
- The adsorption of the essential oil of *Eugenia caryophyllus* on the copper in a solution of 2 M HNO_3 is done according to the Langmuir adsorption isotherm, with a high correlation coefficient. The adsorption process is an endothermic process and stable.
- The efficiency determined by electrochemical polarization inhibitors, Electrochemical impedance spectroscopy, and gravimetric values are in good agreement.

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