

Adsorption and Inhibiting Copper Corrosion in A Nitric Acid Solution by Artemisia Essential Oil

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Abstract

The inhibitory action of the Artemisia essential oil (AEO) on the corrosion of copper in a 2 M HNO₃ solution in the temperature range from 283 to 313 K was measured by gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The results obtained show that the AEO inhibits the corrosion of copper in a solution of 2M HNO₃ and that the effectiveness of inhibition increases with increasing concentration of the inhibitor,

and decreases proportionally with temperature.

It appears from the study of potentiodynamic polarization that the essential oil tested is a mixed type inhibitor with a cathodic predominance with its adsorption on the copper surface following the Langmuir adsorption isotherm. The kinetic data for dissolution were also studied.

Keywords: copper, corrosion, inhibition, essential oil of Artemisia, adsorption.

1. Introduction

The use of inhibitors is one of the usual methods of protection of metallic materials against corrosion in acidic environments. Among these applications, we can cite the acid pickling, industrial acid cleaning and acid descaling. Due to the aggressiveness of most acid solutions, inhibitors are generally employed to block or reduce the corrosive attack of metallic materials. The available evidence indicates that most organic compounds act by the phenomenon of adsorption to the metal surface.

The adsorption mechanism of the inhibitor is influenced by the nature of the surface charge and the metal, by the type of electrolyte and its aggressiveness and by

the chemical structure of the inhibitors. The main types of interactions between the inhibitor and the metal surface are physical adsorption and chemisorption. The adsorption of the inhibitor is linked to the presence of heteroatoms such as nitrogen, oxygen, phosphorus, sulfur and/or triple bonds or aromatic rings in their molecular structure. The good results obtained with the use of natural organic compounds in inhibiting the corrosion of metals in acidic media, prompted us to test the inhibitory action of other organic compounds.

However, most inhibitors used are toxic and cause a lot of environmental damage. In this context, we are interested in the application of non-toxic natural products as corrosion inhibitors. These products are

used as extracts or as essential oils. We include the oils of rosemary [1, 2], clove [3], mint pulegone [4], henna, pyrrolidine, irniine, thyme [5, 6, 7 and 8], ginger [9], bbugaine [10].

In the literature authors use natural products such as aqueous extracts of rosemary as a corrosion inhibitor of the alloy of aluminum and magnesium [11], extracts of prickly pear (*Opuntia*) as a corrosion inhibitor of aluminum [12] and honey as a corrosion inhibitor for steel [13]. Essential oils are known and have been used for over 7000 years. They consist exclusively of odorous volatile terpene molecules found in plants and aromatic trees.

The aim of this study is the study of the inhibition of the corrosion of copper in a 2M HNO₃ by the nontoxic essential oil of *Artemisia* by gravimetric, electrochemical measurements, and finally electrochemical impedance spectroscopy.

2. Materials and Methods

2.1. Extraction of essential oil of *Artemisia* (AEO)

Artemisia herba alba was collected in the region of Agadir, Morocco. The aerial parts of the plant are air dried in the laboratory at room temperature.

The essential oil was obtained by steam distillation of water using a Clevenger-type distiller for 2h30min. The yield of essential oil of *Artemisia* is 1.1%. 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.

2.2. Preparation of the solution

The 2 M HNO₃ solution was prepared by dilution of the nitric acid of analytical grade 67% with distilled water. Test solutions were freshly prepared before each experiment. Experiments were conducted in triplicate to determine reproducibility.

2.3. Gravimetric measurements

Gravimetric tests were conducted by maintaining the desired temperature of the electrolyte with a FRIGITHERM thermostat. The electrolyte volume was 30mL. The samples are in rectangular form with the surface area of 9.6 cm². Prior to measurements, they undergo a mechanical polishing with abrasive paper of different particle size up to 1200, followed by degreasing with acetone, and rinsing with distilled water and drying in air. Each value is the average of at least three tests.

2.4. Measures electrochemical

The electrochemical experiments were performed in a Pyrex cell, equipped three electrodes: copper as the working electrode in the form of discs cut with a geometric area of 1 cm², platinum as a counter electrode and the saturated calomel/ECS electrode as the reference electrode. The copper disc was abraded with abrasive paper of different particle size up to 1200, degreased with acetone, rinsed with distilled water and dried before each test. The measurements are performed using a potentiostat-galvanostat PGZ100,

associated with the "voltmaster4" software.

The current-potential curve is obtained in potentiodynamic mode, 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 of the electrochemical impedance spectroscopy (EIS) were performed with the same electrochemical system. The frequencies between 100 KHz

and 10 mHz were superposed on the corrosion potential. The diagrams given in the impedances are Nyquist representation.

3. Results and Discussion

3.1. AEO Analysis

The analysis of the chemical composition (figure 1) of the essential oil of *Artemisia herba alba*, shows the presence of alpha thujone chemotype and camphor. Table 1 summarizes the main constituents of the essential oil.

Table 1: Constituents of the essential oil of Artemisia

Compound Name	No.	Retention time	Percentage (%)
camphene	1	9.36	3.57
1,8-cineole	2	12.64	9.28
alpha thujone	3	15.56	25.99
beta thujone	4	15.98	16.01
camphor	5	16.97	28.96
myrtenal	6	21.31	6.44

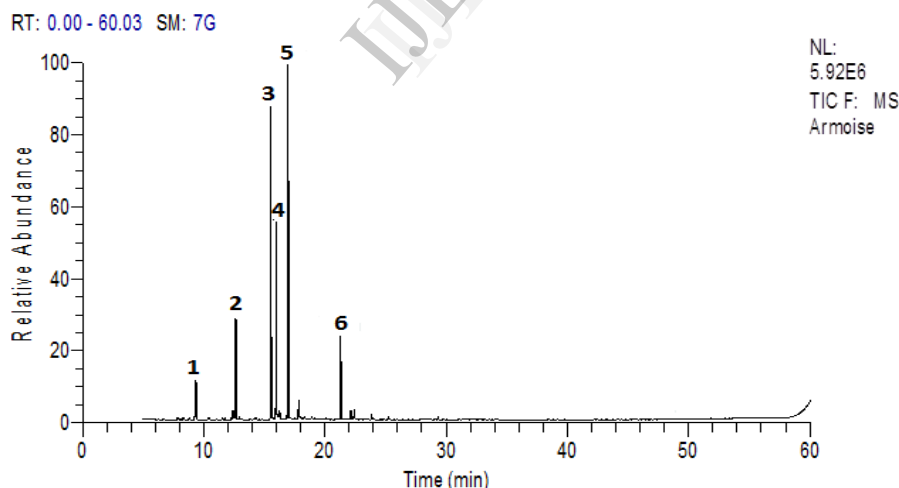


Figure 1: Chromatogram of Artemisia herba alba

3.2 Effect of concentration

3.2.1 The potentiodynamic polarization measurements

The figure 2 shows the anodic and cathodic polarization plots of copper immersed in 2

M HNO₃ at 293 K in the absence and presence of various concentrations of the inhibitor used. Electrochemical data, the corrosion potential (E_{corr}), the cathodic (β_c) and anodic (β_a) Tafel slopes, and the corrosion current density (I_{corr}) are listed

in Table 1. The effectiveness of inhibition (%) is calculated by:

$$IE \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100$$

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

Under the experimental conditions used, the cathodic branch represents the release of hydrogen and the anodic branch represents the dissolution of copper.

Inspection of these results shows that the density of corrosion (I_{corr}) decreased in the presence of the inhibitor. This behavior reflects its ability to inhibit corrosion of the copper in a solution of 2M HNO_3

The anodic and cathodic current densities were reduced (Figure 2), indicating that the Artemisia essential oil (AEO) reduces both the anodic and cathodic reactions due to its adsorption on the metal surface. It is suggested that AEO acts as a mixed type corrosion inhibitor for copper in a 2M solution of HNO_3 [14].

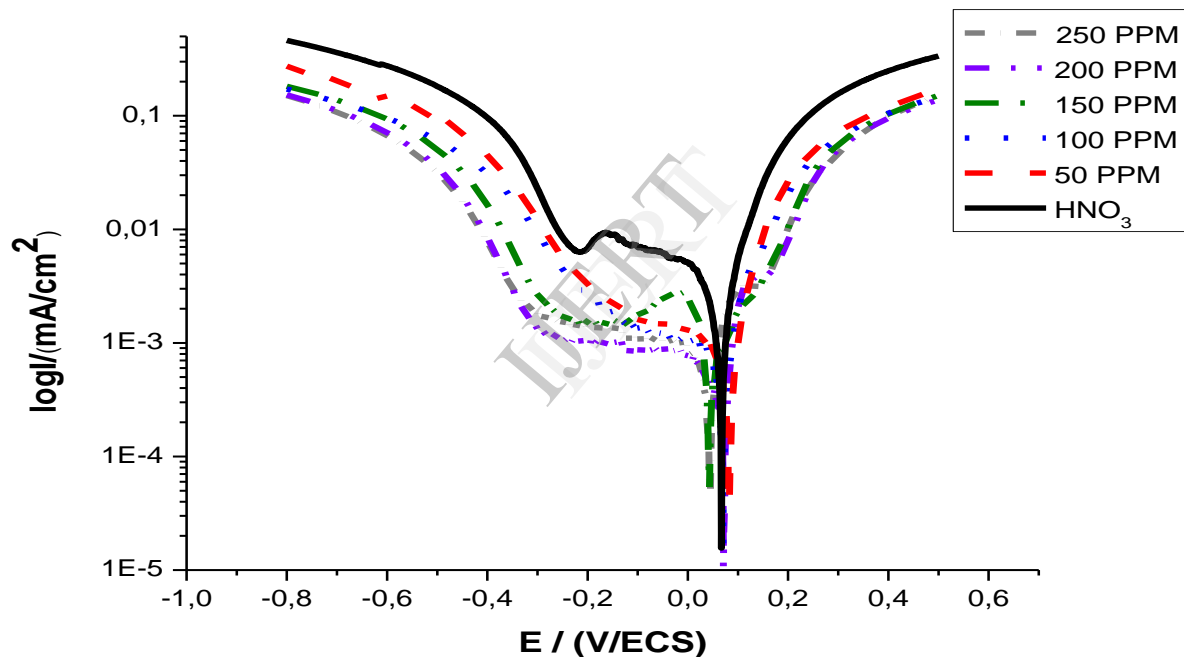


Figure 2: Potentiodynamic polarization curves of copper in 2 M HNO_3 in the absence and presence of Artemisia essential oil at different concentrations at 25 °C.

Table 2: inhibitory efficiency and electrochemical parameters of copper in 2M HNO_3 without and with addition of Artemisia essential oil at different concentrations at 25 °C

Inhibitor	C_{inh} / (ppm)	E_{Corr} / (mV / SCE)	I_{Corr} / (mA / cm^2)	β_a / (mV)	$-\beta_c$ / (mV)	IE%
Blank	---	65.2	2.1741	77.0	349.5	---
Artemisia essential oil	50	58.5	1.1267	49.8	320.6	48.18
	100	64.9	0.9842	71.4	332.7	54.73
	150	60.2	0.4467	76.5	329.8	79.45
	200	41.8	0.1867	83.0	335.6	91.41
	250	42.2	0.1745	96.0	334.2	91.97

It also appears from Tafel slopes (Figure 2, Table 2) that the adsorption of the inhibitor moving slightly the corrosion potential (E_{corr}) in the most negative direction contrary to the blank, which means that the reduction of the cathodic reaction is the main effect of the corrosion inhibitor [15]. Therefore, these results indicate that AEO acts as an inhibitor of the mixed type with a predominant control of the cathodic reaction [16].

The modes of inhibition of organic inhibitors are classified into three categories [17, 18 and 19]: geometric locking effect of the adsorbed inhibitory species, blocking of the active sites by the adsorbed species, and the electro-catalytic effect of the inhibitor or the by-products of its reactions. It was suggested that the first mode of inhibition is the result of reducing the reactive area on the surface of the corrosion resistant metal, while the other two modes of inhibition are due to changes of the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. Cao explained that if the shift of the corrosion potential due to the addition of an inhibitor on the interface is negligible, the inhibition is probably caused by the geometrical locking inhibitory species adsorbed on the surface of the metal [20]. From the results of polarization, it can be concluded that the inhibition by AEO is caused by geometrical locking effect. The Tafel slopes (Figure 2) show that the addition of

the inhibitor to the solution of 2M HNO_3 does not change the mechanism of evolution of hydrogen and the reduction of H^+ ions at the surface of the copper, which occurs primarily by a charge transfer mechanism [21].

The effectiveness of inhibition increases with the concentration of inhibitor to achieve 91% to 250 ppm Artemisia essential oil by lowering the current density of a value of 2.1741 mA/cm^2 to a value of 0.1745 mA/cm^2 .

3.2.2 Measurements of electrochemical impedance spectroscopy

The Nyquist representations for copper in 2 M HNO_3 solution in the absence and presence of different concentrations of AEO are given in figure 3. The impedance spectra are in the simple form of semicircles, and the semicircles diameter increases with increasing concentration of inhibitor. The presence of a single half-circle indicates that the charge transfer occurs at the electrode-solution interface, and the transfer process of the reaction of copper corrosion in the presence of the inhibitor does not alter the dissolution mechanism [22, 23]. The dielectric parameters are given in Table 3. The R'_T values increase with increase in the concentration of AEO while the C_{dl} values decrease. Higher R'_T values may suggest the formation of a protective layer on the surface of the electrode [24].

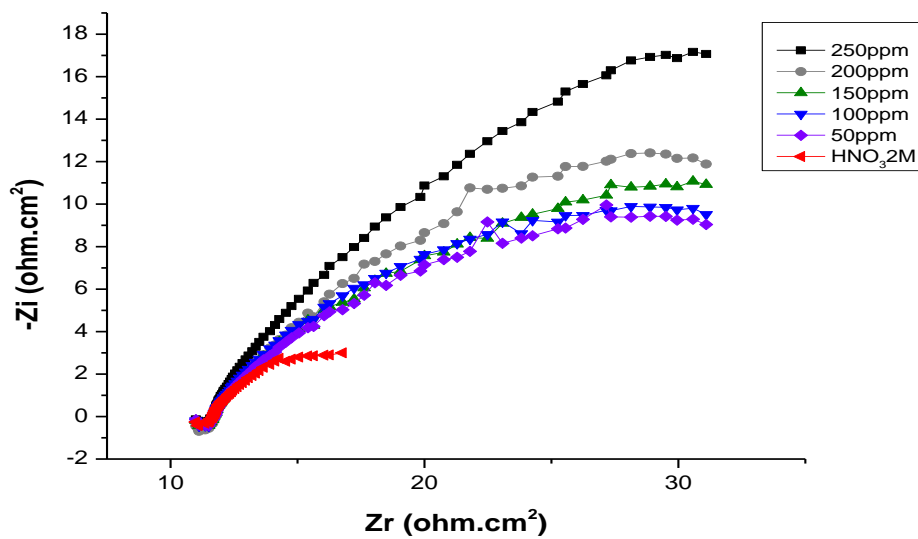


Figure 3: Nyquist Representation of copper in 2M HNO₃ to different concentrations of AEO to Ecorr

Table 3: Electrochemical characteristics of the impedance diagram of copper with and without addition of inhibitors in 2M HNO₃, at the corrosion potential

inhibitors	Concentration in ppm	R _T / ohm.cm ²	f _m / Hz	C _{dl} / μF/cm ²	E%
Blank	0	18.71	22.89	371.5	-----
Artemisia essential oil	50	35.67	12.47	357.65	47.55
	100	40.75	12.78	305.54	54.08
	150	66.89	9.28	256.21	72.03
	200	180.52	5.50	160.04	89.63
	250	211.35	5.06	148.74	91.15

The inhibitory effectiveness was determined by:

$$E \% = \frac{R'_T - R_T}{R'_T} \times 100$$

Where R_T and R_T' are respectively the resistance of the charge transfer copper in 2M HNO₃ in the absence and presence of inhibitor to E = 65 mV / SCE.

The values of charge transfer resistance (R_T) were calculated based on the difference in impedance between the upper and lower frequency values.

The double layer capacity (C_{dl}) and frequency (f_{max}) at which the imaginary

component of the impedance is maximum are represented by:

$$C_{dl} = \frac{1}{2 \pi f_{max} R_T}$$

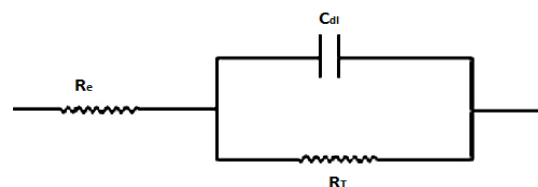


Figure 4: Equivalent circuit used for modeling the impedance diagrams made at the corrosion potential.

The C_{dl} values are noted to be below those of the blank, thereby confirming

the adsorption of inhibitor onto the metal surface. This forms a double electronic shell [25].

These results are in good agreement with those obtained by polarization where AEO turns out to be a good inhibitor for copper in acidic medium 2M HNO₃ with an efficiency of 91%.

The said equivalent circuit of Randles used to study the impedance is given in Figure 4. The resistance R_e of the circuit corresponds to the resistance Randles of finite conductivity of the electrolyte. The charge phenomenon of the electrode / solution interface causes the appearance of a capacitive current (represented by C_{dl}). The charge transfer resistance R_T is identified at the charge transfer resistance [26].

3.2.3 Gravimetric measurements

The weight loss measurements were carried out at 293 K in the absence and in the presence of different concentrations AEO samples after immersion in the etching solution of 1h. The efficiency of inhibition, IE (%), and the corrosion rate were calculated using the equations:

$$W = \frac{m_1 - m_2}{A t}$$

$$IE (\%) = \left(\frac{w - w'}{w} \right) \times 100$$

Where m_1 and m_2 are the weight losses (mg) before and after immersion in the test solutions, A is the sample surface (cm²), t is the exposure time (h), and w and w' are, respectively, the corrosion rates of copper in 2 M HNO₃ without and with addition of inhibitor (mg.cm⁻².h⁻¹).

The values of the efficiency of inhibition, IE (%) obtained by using the method of

weight loss for the different concentrations of AEO are summarized in Table 4. It is very clear that the AEO inhibits corrosion of copper in a solution of 2M HNO₃, since the corrosion rate (W) continuously decreases with increasing inhibitor concentration at 293 K, and the maximum efficiency (88.89%) was obtained at 250 ppm. The comparison shows that the three techniques EI (%) obtained by using the impedance technique are comparable, and are parallel to those obtained by the methods of losing weight and polarization (Figure 5).

Table 4: Corrosion rate and inhibitory efficiencies of copper in 2 M HNO₃ with and without addition of the Artemisia essential oil at different concentrations at 25 °C.

Inhibitor	Concentration (ppm)	W (mg/cm ² .h)	EI (%)
Blank	0	0.09375	----
Artemisia essential oil	50	0.05208	44.45
	100	0.0416	55.63
	150	0.03125	66.66
	200	0.0109	88.37
	250	0.010416	88.89

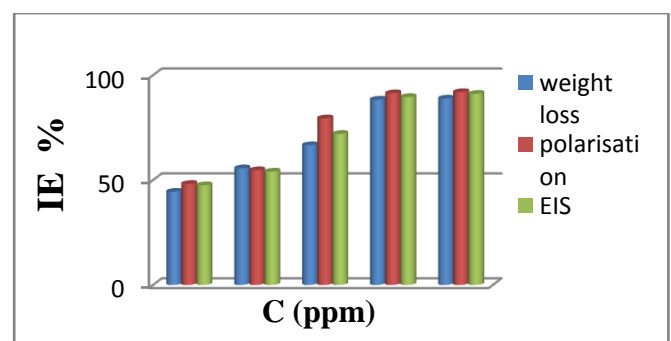


Figure 5: Comparison of the efficacy of inhibition (IE%) obtained by the use of weight loss, polarization and impedance measurements.

3.3 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 [27].

The I_{corr} value was obtained by extrapolating the Tafel slopes in experiments conducted at 283, 293, 303,

and 313 K. The polarization curves for copper in a 2M HNO_3 solution in the temperature range (273-313 K) are shown in Figures 6 and 7, with and without 250 ppm of AEO. The various numerical values of the variation of the corrosion current density (I_{corr}), the corrosion potential (E_{corr}), cathodic Tafel slope (β_c), and anodic Tafel slope (β_a) to 250 ppm of inhibitor (AEO) all the studied temperatures are shown in Table 5.

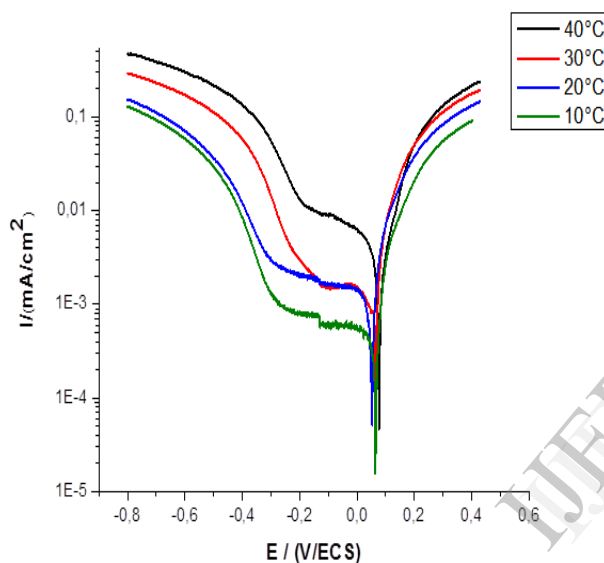


Figure 6: Effect of temperature on the anodic and cathodic reactions of copper in 2M HNO_3 .

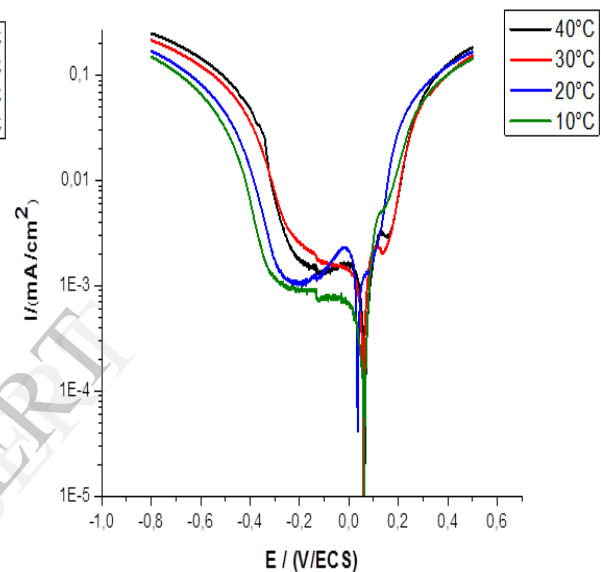


Figure 7: Effect of temperature on the cathodic and anodic reactions of copper in 2M HNO_3 with 250 ppm of Artemisia essential oil.

Table 5: Electrochemical parameters of copper in 2 M HNO_3 without and with 250 ppm of AEO, at different temperatures.

Inhibitor	Temperature / (K)	E_{Corr} / (mV / SCE)	I_{Corr} / (mA / cm^2)	β_a / (mV)	$-\beta_c$ / (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	---
250 ppm AEO	283	73.6	0.0787	101.4	102.5	94.88
	293	63.6	0.1268	77.3	124.1	93.47
	303	65.7	0.3053	68.5	114.6	89.79
	313	82.5	0.6826	59.6	211.2	81.30

In the absence and in presence of AEO, the I_{corr} value increases with increasing

temperature. It is also evident that the AEO 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 (weak bonds). This type of temperature-sensitive links cannot fight effectively against corrosion when the temperature increases [28].

In the case of the acid corrosion, many authors [29] 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 relationships:

$$I_{\text{corr}} = K \exp(-E_a / RT)$$

$$I = K' \exp(-E'a / RT)$$

Where k and k' are constants (Arrhenius pre-exponential parameters), and E_a 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 E_a to both the presence and absence of the inhibitor. The figure 8 shows the Arrhenius coordinates plot in the corrosion rate of copper in 2M HNO_3 in the absence and presence of Artemisia essential oil to 250 ppm.

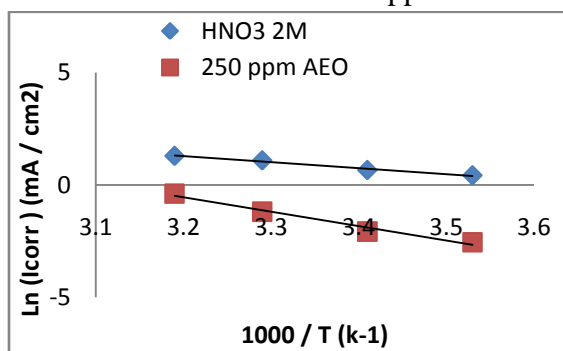


Figure 8: Arrhenius diagram of the dissolution of copper in 2M HNO_3 at different temperatures with and without inhibitor.

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

Table 6: Activation energy of dissolution of copper in 2M HNO_3 with and without inhibitor.

Sample	E_a / (kJ / mol)
Blank	19.38
Artemisia essential oil	31.29

From the results of Table 6 it is clear that in the presence of inhibitor the activation energy increases, so that IE% decreases as the temperature increases. This behavior demonstrates the physisorption phenomenon of the inhibitor to the metal surface. The rate of recovery, lower at higher temperatures suggests that at these temperatures, the rate of destruction of the film physically adsorbed increases faster than its rate of formation.

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 [28, 29].

The values of the activation energy obtained from the Arrhenius slope is 19.38 kJ mol^{-1} in the absence of inhibitor, this value is in agreement with the literature [30], and at a concentration of 250 ppm AEO, when the rate of recovery is maximum, and the value of the activation energy in the presence of this oil is 31.29 kJ mol^{-1} . This confirms the physical adsorption AEO by the formation of an effective 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 [31]:

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

Where h is Planck's constant, N is the Avagadro number, ΔS^* is the entropy of activation and the ΔH^* is the activation enthalpy. Figure 9 shows plots of $\ln(I_{\text{corr}} / T)$ versus $1 / T$. Straight lines are obtained with a slope of $-\Delta H^* / R$ and an intercept of $(\ln R / N h + \Delta S^* / R)$, from which the values of ΔS^* and ΔH^* can be calculated, these values are in Table 7.

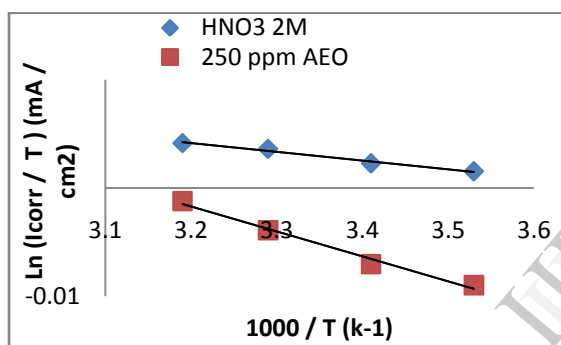


Figure 9: Relationship between $\ln(I_{\text{corr}} / T)$ and $1000 / T$ at different temperatures

Table. 7: The values of the activation parameters ΔH^* and ΔS^* of copper in 2M HNO_3 in the absence and presence of 250 ppm of Artemisia essential oil at $T = 293\text{K}$

Inhibitor	ΔH^* (KJ / mol)	ΔS^* (J / $\text{mol}^{-1} \cdot \text{K}^{-1}$)
Blank	10.34	-245.01
AEO (250 ppm)	38.94	-232.04

Inspection of these data revealed that the thermodynamic data (ΔS^* and ΔH^*) for the reaction of copper dissolution in 2 M HNO_3 in the presence of inhibitor is greater than in the absence of inhibitor.

The positive sign of ΔH^* reflects the endothermic nature of the process of dissolution of the copper, which suggests that the slow dissolution of the copper is in the presence of inhibitor [32]. By comparing the values of the activation data ΔS^* entropy in Table 7, it is clear that the activation entropy decreases negatively to a great extent in the presence of AEO more than absence of the inhibitor, thus reflecting the formation of a stable layer of controlled inhibitor on the surface of copper [33].

Moreover

$$\Delta G^* = -R \times T \times \ln(55.5 \times K)$$

$$K = \Theta / C \times (1 - \Theta) \quad (10)$$

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 $\Delta G^* = -58.26 \text{ kJ / mol}$, indicating spontaneous adsorption of inhibitory molecules on the surface of copper. ΔG^* value obtained indicates that the adsorption occurs by the mechanism physisorption.

3.3.1 Adsorption isotherm

The adsorption on the surfaces of corrosion has never reached a real equilibrium and tends to reach a state of adsorption equilibrium. However, when the corrosion rate is sufficiently small, the stationary state of adsorption tends to become a quasi-equilibrium state. In this case, it is reasonable to consider that the adsorption thermodynamic quasi-equilibrium isotherms using appropriate balances [34]. The adsorption behavior provides information on the interaction between the

adsorbed molecules and their interactions with the surface of the electrode [35].

It has been reported that the adsorption of the inhibitor molecules depends on a variety of factors, for example the presence of functional groups (or electron donor or withdrawal), steric factors, the distribution of load on the donor atom, the π orbital nature of electron donors, the nature of the metal substrate, and the type of interaction between the organic molecules and the metal surface [36]. The adsorption isotherms of temkin, frumkin and langmuir were used to represent the adsorption AEO 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.

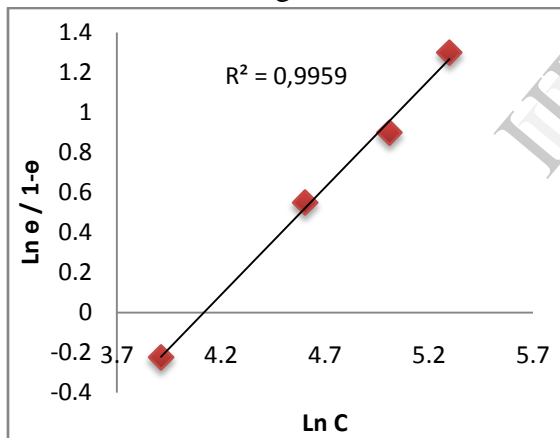


Figure 10: Model Langmuir isotherm for the adsorption of the inhibitor on the surface of the AEO copper in 2 M HNO_3 at 25 °C.

The curve representing $\ln(\theta / 1-\theta)$ as a function of $\ln[C]$, where C is the concentration of inhibitor, is a straight line (Figure 10) indicating that the adsorption of the inhibitor on the surface of the copper plate is according to the Langmuir model:

$$\ln(\theta / 1-\theta) = K \ln [C]$$

The strong correlation ($R^2 = 0.965$) for a portion of the field of isothermal Langmuir adsorption inhibitor confirms the validity of this approach.

Based on the Langmuir isotherm, we can put an approach to the representation of adsorption phenomena, which is based on three assumptions, explaining that the adsorption is localized and does not give rise to the formation of a monolayer, and all sites are equivalent and the surface is uniform, and that there is no interaction between the adsorbed molecules which allows to consider the adsorption energy as constant [37].

Conclusion

The following conclusions can be drawn from this study:

- AEO is an effective inhibitor of the corrosion of copper in a solution of 2M HNO_3 . AEO efficiency increases with the concentration to achieve 91% to 250 ppm.

- The study results suggest that AEO behaves as mixed type inhibitor with dominant cathodic reaction control.

- Results from electrochemical impedance spectroscopy indicate that the adsorption of AEO on the surface of the copper increases the strength and reduces the transfer capacity of the double layer.

- The adsorption of the copper AEO in a 2M solution of HNO_3 is done according to the Langmuir adsorption isotherm, with a high correlation coefficient. The adsorption process is a stable endothermic process.

- The efficiency determined by electrochemical polarization inhibitors, Electrochemical impedance spectroscopy,

and gravimetric values are in good agreement.

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