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# Gravimetric, Electrochemical, and Surface Morphological Studies of *Ammodaucus Lecotrichus* Essential Oil as Corrosion Inhibitor for Copper Surface in Hydrochloric Acid Medium

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**Abstract**- The aim of this work is the study of the inhibition corrosion of copper in hydrochloric acid solution 2M using essential oil of *ammodaucus leucotrichus* Coss. & Dur. noted (AEO). Its protective ability is evaluated by weight loss measurements, electrochemical impedance spectroscopy (EIS) and polarization curves, at different concentrations of the oil (0-3000 ppm) and by varying the temperature of the solution (298-328K). The polarization curves highlight the cathodic character of this eco-friendly inhibitor. However, the corrosion rate was reduced when the concentration of AEO is increased and achieves about 70% after 6h immersion in corrosive media containing 3000 ppm of AEO. This important protection ability is relied to the formation of a protective film over the metal, which its adsorption is governed by the Langmuir isotherm model. The negative values of the free standard adsorption energy  $\Delta G_{ads}$  confirm the spontaneity of the reaction. Interestingly, scanning electron microscopy (SEM) analysis underlines a remarkable enhancement on the surface of copper exposed to the corrosive media, in presence of AEO and hence, its efficiency as an ecofriendly inhibitor for copper surface.

**Keywords-** Ammodaucus leucotrichus essential oil; Corrosion inhibitor; Copper; Weight loss; electrochemical impedance spectroscopy

# **1. INTRODUCTION**

Corrosion is an important economic, environmental and safety issue. It affects many structures, particularly metallic materials [1, 2]. This is one of the main causes of the alteration and destruction of most installations and equipment. Corrosion phenomena depend on a large number of factors that occur not individually, but in more or less complex relationships with each other: the nature and structure of the material, surface treatments [3], the environment and its chemical characteristics, temperature, the hydrodynamic regime to which the material is subject. The aggressive medium constitutes a particularly favourable environment for the deterioration of metallic materials. The study of the acid corrosion inhibition of these materials is therefore a very attractive field of research [4] because of the wide use of acidic solutions in the industry, especially in metal pickling baths and for the cleaning of industrial installations. In recent years, the field of corrosion has expanded very rapidly, and is increasingly moving towards the development of non-toxic, non-polluting and stable organic molecules. In terms of protection, organic inhibitors are an original way to fight against corrosion of metals in an aggressive environment [5-7]. Compounds containing unsaturated bonds and /or polar atoms such as oxygen (O), nitrogen (N) and sulfur (S) are often good inhibitors of corrosion of metals [8-10]; in particular copper in the acidic medium, their mode of action has been the subject of several studies [11-20]. Copper is a relatively noble metal often used for the piping of heating or cooling systems [21] and in the electronics industry [22-24], its resistance to corrosion in a ventilated environment is due to the formation of a protective film; the nature of this film depends on the composition of the medium considered. Despite this self-protection property, this metal can undergo severe corrosion in aerated acid medium or in polluted industrial environments containing chloride ions, sulphates or nitrates [24]. In the literature, most studies that are done consider that chloride ions are responsible for the dissolution of cuprous materials

and its alloys in hydrochloric acid [25-28]. These factors prompted researchers to work on the development of copper alteration to the aggressive action of these acids, the mechanisms of formation of corrosion products, as well as the types of corrosion. It is in this context that comes this work which is interested in the study of the inhibitory action of the essential oil of *ammodaucus leucotrichus* Coss. & Dur. (AEO) on the copper in hydrochloric acid 2M medium. This compound has the advantage of not being toxic and also gave satisfactory results for inhibition of corrosion of steel and tinplate in acidic and alkaline medium [29-31]. To our knowledge, until now, no work has been reported on the inhibitory effects of essential oil of A. leucotrichus on copper in 2M hydrochloric acid solution. For this reason, corrosion parameters were determined using the gravimetric method, electrochemical impedance, and electrochemical polarization measurements. The surface is characterized by the use of electron microscopy (SEM) spectroscopy.

## 2. EXPERIMENTAL

#### 2.1. Extraction of A. leucotrichus essential oil (AEO)

The whole plant was collected from Beni-Abbes, Province of Béchar (Southwest of Algeria). The fruit parts of *A. leucotrichus* (150 g) were submitted to water-distillation for 3 hours, using a Clevenger-type apparatus. At the Natural Products Laboratory (Biology Department, University of Tlemcen, Algeria), a voucher sample was put under accession No. A. 1918. The essential oil was dried over anhydrous sodium sulfate and stored in amber vials at +4°C.The extractions were performed in triplicate.

# 2.2. Test solutions

The inhibition tests were conducted on the commercial pure copper in 2M HCl solution, at different concentrations of AEO (500-3000 ppm). For each test, freshly prepared test solutions were used. All the experiments were conducted in solutions opened to air, at 298K. A thermostated bath was used to maintain the temperature of the solution at the desired value.

#### 2.3. Weight loss measurements

Gravimetric experiments were carried out in a glass cell placed in a thermostat water bath. The aggressive solution volume was 100 mL. Rectangular copper specimens with a surface area of 7.6 cm<sup>2</sup> were used. The sheets were abraded successively with emery paper graduate 400, 600, 1200, rinsed with bi-distillated water, degreased with acetone, washed again with bi-distilled water, then dried using a stream of air and weighted before their immersion into the test solution. After 6h of immersion at 298K, the samples were rinsed, dried and weighted using an analytical balance. We determined the efficacy of inhibition from the weight loss measures collected at the end of specific periods of time in the existence and nonexistence of the inhibitor according to the equation (1) [32]:

$$E\%=100\times\frac{Wo-W}{Wo}$$
(1)

where W<sub>0</sub> and W are the corrosion rates in the absence and presence of inhibitor respectively.

## 2.4. Electrochemical measurements

The electrochemical measurements were carried out in a double-wall thermostated Pyrex cell, equipped with a conventional three-electrode assembly: a platinum electrode, as an auxiliary electrode, a saturated calomel electrode (ESC) as reference electrode and a copper as the working electrode. The latter is in the form of a disc where only a part of  $0.5 \text{ cm}^2$  is exposed to the aggressive solution. The rest being covered with resin. The electrochemical measurements were performed using the Autolab measuring system which includes the Potentiostat-Galvanostat type (PGZ 201N), a computer and the Nova1.9 software. The electrochemical impedance spectra (EIS) were obtained at the corrosion potential after 1 h of immersion at zero current, in a frequency range from 100 KHz to 10 MHz, with a sinusoidal potential perturbation of 10 mV. The electrode was polished with emery paper before each measure and was directly taken into the test solution. In the potentiodynamic process, intensitypotential curves E = f(I) or polarization curves of the metal / solution interface were provided. The potential applied to the sample varies continuously from -700 to 500 mV vs. SCE with a scan rate of 0.5 mV/s from cathodic to anodic direction. The intensity of the current was measured between the working electrode and the counter electrode. Before the drawing of these curves, the working electrode was maintained at its abandoning potential, into the corrosive solution for one hour to define the steady state open circuit potential (E<sub>ocp</sub>).

#### **2.5 Surface Analysis**

The surface morphologies of the copper samples were examined by scanning electron microscopy (SEM) Quanta 250 FEI instrument, equipped with a field emission filament using an acceleration voltage of 5 KV and a working distance of 10 mm. Before analysis, the samples were taken out of the HCl solution, cleaned with bidistilled water and dried carefully using a stream of air.

## **3. RESULTS AND DISCUSSION**

## 3.1. Chemical Characterization of the essential oil

AEO was obtained by hydrodistillation and characterized using GC-MS (RI), and <sup>13</sup>C NMR spectroscopic analysis. In total, 11 components accounting for 97.18 % of the oil were identified. The chemical composition of the oil was highly dominated by perillaldehyde (87 %). Limonene (8.2%) was also identified (Table1) [33].

#### **3.2.** Weight loss tests

The values of corrosion rate (w) and inhibition efficiency (E%) obtained from gravimetric measurements, at different concentration of AEO and at 298 K are listed in Table 2.

Components <sup>a</sup>	RIa <sup>b</sup>	RIp <sup>c</sup>	Amount	Identification mode
α-Pinene	930	1012	0.3	RI, MS, 13C-NMR
β-Pinene	973	nd	0.1	RI, MS
Myrcene	980	1161	0.1	RI, MS
δ-3-Carene	1005	1150	0.5	RI, MS, 13C-NMR
p-Cymene	1011	1271	0.1	RI, MS
Limonene	1021	1203	8.2	RI, MS, 13C-NMR
Cuminaldehyde	1220	1782	0.1	RI, MS
Perillaldehyde	1249	1782	87.0	RI, MS, 13C-NMR
Perillyl alcohol	1270	2010	tr	RI, MS
Methylperillate	1369	1866	0.6	RI, MS
γ-Decalactone	1423	nd	0.1	RI, MS
Total (%)			97.1	_

Table 1. Chemical composition of the fruit oil of A. leucotrichus

<sup>a</sup>Order of elution and percentages of individual components are given from anapolar column (BP-1), RIa<sup>b</sup> : retention indices from anapolar column, RIp<sup>c</sup> : retention indices on polar column. tr = trace level (<0.05%), nd = not determined.

Table 2.	Corrosion	parameters	for	copper i	in 2M	HCl	solution	in the	presence	of	different
concentra	ations of Al	EO at 298 K	, afte	er 6h im	mersio	n					

Conc. (ppm)	Corrosion rate (mg/cm <sup>2</sup> h)	E (%)	Surface coverage ( $\theta$ )
HCl 2M	0.0353		
500	0.0252	28.38	0.28
1000	0.0209	40.65	0.40
2000	0.0145	58.84	0.58
3000	0.0105	70.06	0.70

It is clear from the data that the extracted AEO decreases the corrosion rate of copper metal in 2M HCl solution by increasing the concentration oil from 500 to 3000 ppm. The enhancement of the inhibition efficiency is about 70%, reveals the importance of using of AEO as an efficient corrosion inhibitor. Note in this context that Kalada et al. [6] found an efficiency of inhibition of copper corrosion equal to 71% for the extract of *Aloe Vera Barbadensis* Gel in a 2M HCl medium.

#### 3.3. Potentiodynamic polarization measurements

The potentiodynamic polarization plots of copper in 2M HCl solution without and with the addition of different concentrations of AEO are shown in Fig. 1.



**Fig. 1.** Polarization curves of copper immersed in 2M HCl in the absence and in the presence of different concentrations of AEO at 298 K.

In absence of AEO, the anodic currents display distinct regions: At first, the current increases and then stabilizes. This suggests a limited diffusion rate, which is ascribed to the mass transport of chloride ions (Cl) to the interface [34]. Then, a Tafel region is detected, extending to the peak current density, towards potentials close to -50 mV due to the dissolution of copper into Cu<sup>+</sup>. A region of decreasing currents is noticed, until a minimum is reached, due to the formation of CuCl [35,16]. However, it is observed that an extra increase in current density leads to a limit value following the formation of CuCl<sub>2</sub> [16]. This latter is responsible for the corrosion of copper, either because of its dissolution in the bulk solution or of its new oxidation to cupric ions [36,37,25]:

$$\operatorname{CuCl} + \operatorname{Cl}^{-} \to \operatorname{CuCl}_{2}^{-} \tag{2}$$

$$\operatorname{CuCl}_{2 \operatorname{ads}} \rightarrow \operatorname{Cu}^{2+} + 2\operatorname{Cl}^{-} + e^{-} \tag{3}$$

The cathodic polarization curve exhibits a substantially linear variation from -0.48 V/SCE to -0.65 V/SCE, which implies the existence of a kinetically controlled domain. Then, a diffusion plateau between -0.7 and -1 V/SCE, is recorded and attributed to the diffusion-controlled reduction of dissolved oxygen [37,25].

The next equation gives the cathodic reaction of corrosion in HCl [37-39]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}$$

A small change of the corrosion potential to cathodic one is observed by the addition of various concentrations of inhibitor, which is followed by a reduction in cathodic current. Moreover, we observe that the anodic polarization curves are not so much affected by the presence of this inhibitor, which shows the cathodic nature of the latter. The electrochemical parameters such as: corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ) values, cathodic and anodic Tafel slopes (bc and ba), as well as inhibition efficiency E(%) for all concentrations of the inhibitor in HCl are summarized in Table 3.

The inhibition efficiency (E%) values are calculated from the following equation:

$$E(\%) = \left(\frac{I_{corr} - I_{corr(inh)}}{I_{corr}}\right) \times 100$$
(5)

where  $I_{corr}$  and  $I_{corr}$  are the corrosion current density values calculated by extrapolating cathodic Tafel lines to the corrosion potential in the existence and absence of an inhibitor, respectively.

Conc.(ppm)	Ecorr vs SCE (mV)	icorr (mA cm <sup>-2</sup> )	b <sub>c</sub> (mV dec <sup>-1</sup> )	<b>b</b> <sub>a</sub> ( <b>mV dec</b> <sup>-1</sup> )	E (%)
HCl 2M	-482	0.395	75.03	125.4	
1000	-511	0.135	69.5	153.6	65.38
2000	-500	0.128	63.7	142.5	67.17
3000	-513	0.103	50.9	135.5	73.58

**Table 3.** Corrosion parameters of copper in 2M HCl solution containing differentconcentrations of AEO at 298 K.

In the light of the results presented in this table, we note that the inhibitory potency of the test compound increases with its concentration to reach a maximum value of about 73.6% at a concentration of 3000 ppm.

It's important to notice that Boumezzourh et al. [31] have obtained an efficiency of 81% at 4g/L using *A. leucotrichus* essential oil as a corrosion inhibitor of tinplate in 0.5 M oxalic acid medium, also, the study by Mansouri et al. [30] on the uses of *A. leucotrichus* essential oil as a corrosion inhibitor of mild steel in HCl solution, showed that the AEO exhibited a high inhibition efficiency of 85 % at 3 g/L of the concentration of oil. On the other hand, Shabani et al. [40] were used the extract of *Calligonum comosum* as an inhibitor for copper in 2M HCl, the efficiency was 80 % at the concentration of 0.8 g/L. Recall that the inhibition effect depends on several factors such as: The metal itself, in terms of its composition, and atomic structure [41], the type of the aggressive medium and its concentration, solution temperature [42,43] and the chemical composition of the inhibitor.

#### 3.4 Electrochemical impedance spectroscopy

Fig. 2 displays Nyquist impedance diagrams for a copper electrode, after one hour of immersion time in hydrochloric acid medium, at the inhibitor concentrations of 1000 to 3000 ppm. For sake of comparison, the impedance curve of the copper electrode in HCl was also presented.



**Fig. 2.** Nyquist plots for copper in 2M HCl in the absence and presence of various concentrations of AEO at 298K.

From this figure, it can be noticed that in the absence of inhibitor and at 1000 ppm and 2000 ppm of AEO, the impedance plots underline a Warburg line. This indicates that the corrosion process under these conditions is governed by a diffusion phenomenon, relied to a mass transport during the copper dissolution [38].



**Fig. 3.** Electrical equivalent circuit proposed for modeling the Nyquist diagram: (a) Presence of a diffusion phenomenon, (b) Presence of a simple capacitive loop.

The equivalent circuit used to model the impedance diagram is composed of the resistor of the electrolyte  $R_e$ , in series with the charge transfer resistor  $R_{tc}$  and W (which is a term

corresponding to the semi-infinite diffusion) which are in parallel with the double layer capacitance  $C_{dl}$ . A constant phase element (CPE) replaces the  $C_{dl}$  for accurate simulation (Fig. 3a).

At a concentration of 3000 ppm of the inhibitor, the spectrum depicts only a capacitive loop, with a disappearance of the Warburg line. This remarkable difference in the size, as well as the shape of the impedance spectra accompanied by the disappearance of the Warburg impedance and the increase of the capacitive loop, can be attributed to the gradual formation of a film on the copper surface that creates a barrier to the electron exchange with the medium [44]. In this case, the equivalent circuit is presented without the impedance of Warburg (Fig. 3b).

The presence of essential oil significantly reduces the corrosion rate of copper in HCl. Its inhibition efficiency (E%) is calculated according the equation given below [32]:

$$E\% = (1-R_t/R_t) \times 100$$
 (6)

where  $R_t$  and  $R_t$  represent the values of the charge transfer resistance in the absence and presence of the inhibitor, respectively.

The electrochemical parameters such as charge transfer resistance  $R_t$ , double-layer capacitance  $C_{dl}$  derived from Nyquist plots and inhibition efficiency are listed in Table 4.

**Table 4.** Impedance parameters for the corrosion of copper at different concentrations of AEO at 298 K

Conc. (ppm)	$R_t(\Omega cm^2)$	C <sub>dl</sub> (µF.cm <sup>-2</sup> )	E (%)
HCl 2M	421.87	62.72	
1000	671.92	124.37	37.21
2000	1151.7	101.66	63.36
3000	1437.2	197.92	70.64

From this table it can be seen that the charge transfer resistance values in the presence of AEO are superior to that obtained in the absence of the inhibitor molecules. This increase in charge transfer resistance values could be relied to the adsorption of the AEO molecules at the copper-acid interface, blocking the active sites on the copper surface and consequently enhances the corrosion resistance of the copper in acid medium. It is found that by increasing the concentration of essential oil the surface coverage increases as a consequence the inhibition efficiency of AEO against the corrosion of copper surface in HCl increases and reach 70% at 3000 ppm of inhibitor. This value is slightly lower than that obtained by the Tafel extrapolation method (73.8%).

## 3.5 Adsorption kinetic

The inhibition of metal corrosion by organic compounds can be explained either by a physical adsorption or chemisorption [37] and depends on the charge of the metal, its nature, the organic product's chemical structure and the kind of electrolyte. Recovery rate values ( $\theta$ ) for different concentrations of A. leucotrichus essential oil obtained from weight loss measurements (Table 2), in the studied temperature range (298-328K), were used to determine its adsorption isotherm. Generally, it is very difficult to define the adsorption isotherm governing the adsorption of such systems. Thus, different isotherms including Langmuir, Temkin, Frumkin and Frundlich were tested to find the suitable adsorption isotherm. The choice of the suitable isotherm, which is presented graphically as a straight line was determined by the use of the correlation coefficient  $(R^2)$ . The best fit was obtained with the Langmuir isotherm. The Langmuir adsorption isotherm model assumes that there is a fixed number of energetically identical sites on the surface. Each site can adsorb only one chemical entity. Moreover, the model assumes that the interactions between adsorbed particles are negligible and, therefore, the adsorption energy is considered constant [45]. With these assumptions, and for a given temperature, it can be drawn the curve C/ $\theta$  as a function of the concentration C of the inhibitor (Fig. 4).



**Fig. 4.** Langmuir adsorption isotherm plots for copper in 2M HCl at different concentrations of inhibitor obtained by gravimetric analysis.

This plot gives a line indicating that the adsorption of AEO to the surface of the metal follows the Langmuir isotherm. The regression coefficient ( $R^2=0.995$ ) is almost equal to unity and the slope is very close to unity. The values of the thermodynamic parameters were calculated from the modified Langmuir model (Equation 7) [46, 47]:

$$\frac{Cinh}{\theta} = \frac{1}{Kads} + Cinh \tag{7}$$

where  $K_{ads}$  is the equilibrium constant of the adsorption process and  $C_{inh}$  is the inhibitor concentration. The value of the adsorption coefficient ( $K_{ads}$ ), determined by extrapolation of the straight line obtained previously to the axis  $C_{inh}/\theta$  (Fig. 4), then allowed us to access the

$$K_{ads} = \frac{1}{C(sol)} \exp\left(-\frac{\Delta G_{ads}}{RT}\right)$$
(8)

values of the free standard adsorption energy ( $\Delta G_{ads}$ ) from the equation [47]:

where R is the constant of perfect gases in (J.mol<sup>-1</sup>.K<sup>-1</sup>), T is the temperature in K and C (sol) is the concentration of water (1000 g. L<sup>-1</sup>). The values of K<sub>ads</sub> and  $\Delta G_{ads}$  were calculated and are listed in Table 5.

**Table 5.** Thermodynamic parameters for copper in 2M HCl at optimum concentration ofAEO

Inhibitor	K <sub>ads</sub> (L/g)	$\Delta H_a^0 (kJ.mol^{-1})$
AEO	0.7081	-16.26

The negative value of the free energy of adsorption ( $\Delta G_{ads}$ ) confirms the spontaneity of the adsorption process, and the stability of the adsorbed layer on the metal surface. Generally, the  $\Delta G_{ads}$  values, close to -20 kJ.mol<sup>-1</sup> or less negative, are related to electrostatic interactions between the charged molecules and the metal (physical adsorption), while those near -40 kJ.mol<sup>-1</sup> or more negative involve a charge transfer between the organic molecules and the metal surface (chemisorption) [48,49]. In our case and according to **table 5**, the value of  $\Delta G_{ads}$  calculated for the studied inhibitor is negative and below the value -20 kJ.mol<sup>-1</sup>, which indicates that the tested molecules are adsorbed at the metal surface by spontaneous physical interactions (a physisorption mechanism).

# 3.6. Temperature effect on the corrosion inhibition and thermodynamic parameters

The temperature of the corrosive medium is one of the factors which influence the inhibitory efficiency of a compound, as well as the behavior of the substrates in a given aggressive medium. For this, the copper mass loss measurements in HCl without and with the addition of the inhibitor at a concentration of 3000 ppm were performed at a temperature range (298K-328K) for 6h of immersion. The thermodynamic parameters, such as the activation energy  $E_a$  and enthalpy  $\Delta H_a$  of the copper corrosion in hydrochloric acid medium were also calculated.



Fig. 5. Variation of inhibition efficiency of AEO with temperature

As shown in Fig. 5, the inhibition efficiency values decrease by increasing the temperature of the medium. This result may be assigned to the inhibitor molecules desorption of the metal surface at higher temperatures [48].

The variation of the logarithm of the corrosion rate as a function of 1/T for hydrochloric acid solution without and with addition of AEO is shown in Fig. 6.



**Fig. 6.** Arrhenius plots for copper corrosion rates in HCl 2M in the absence and presence of optimum concentration of AEO

The plot is linear, indicating that the Arrhenius law is respected [50, 46, 37]. The energy of activation ( $E_a$ ) which represents the energy necessary for a molecule to possess in order to react [51], is calculated from the slope of this plot (equation 9):

$$W = K + \exp\left(-E_{act}/RT\right) \tag{9}$$

where W is the corrosion rate of copper, K is the Arrhenius pre-exponential factor,  $E_a$  (kJ mol<sup>-1</sup>) is the activation energy, R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the temperature (K).

The values of activation energy, calculated show an energy value equal to 42.96 kJ mol<sup>-1</sup>, in the presence of the AEO essential oil, higher than that obtained in the case of the blank ( $E_a$ =30.2 kJ mol<sup>-1</sup>). According to Majidi et al. [52] Boumezzourh et al. [31] and Merah et al. [53], higher activation energy in inhibiting system compared to the blank is an indication of a physisorption mechanism. On the other hand Szauer and Brand explained that the increase in activation energy can be attributed to an appreciable decrease in inhibitor adsorption on the metallic surface as the temperature increases [54, 55]. On the other hand, Szauer and Brand clarified that the notable decrease in inhibitor adsorption on the metallic surface as the temperature increases in activation energy.

The  $\Delta H_a^o$  values were calculated from the slopes of the plot ln (w/T) = f (1/T) (Fig.7) determined from the following equation:

$$\operatorname{Ln}\left(\frac{W}{T}\right) = -\frac{\Delta H_a^o}{RT} + B \tag{10}$$

where W is the corrosion rate, R is the universal gas constant, T the absolute temperature, B is a constant.



**Fig. 7**. Ln (W/T) vs. 1/T for copper dissolution in 2 M HCl in the absence and presence of 3000 ppm of AEO.

The values of the enthalpy of activation ( $\Delta H_a^o$ ), calculated were positive whatever the medium (Table 6), which implies that the copper dissolution process is endothermic.

**Table 6.** Activation Parameters  $E_a$  and  $\Delta H_a^o$  for the copper dissolution in 2M HCl in the absence and presence of AEO at optimum concentration:

$E_a(kJ.mol^{-1})$	$\Delta H_a^0(kJ.mol^{-1})$
30.2	28.09
42.96	41.07
	E <sub>a</sub> (kJ.mol <sup>-1</sup> ) 30.2 42.96

It is evident from this table that the value of  $\Delta H_a^o$  increases in the presence of AEO compared to the uninhibited solution indicating protective efficiency. This suggests a slow dissolution and therefore a lower corrosion rate of copper.

# 3.7. Surface morphology

The scanning electron microscopy (SEM) was carried out in order to investigate the impact of essential oil on the copper surface morphology. Fig. 8 shows the images taken on the samples after 24 h of immersion at 298 K in 2M HCl in the absence and in the presence of the inhibitor AEO at 3000 ppm.



**Fig. 8.** SEM images of copper (a) 2M HCl solution and (b) 2M HCl solution with optimum concentration of AEO at 298K.

Inspection of the figures indicates that there are significant damages, clear cavities on the surface of copper in the absence of AEO (Fig. 8(a)) than in its presence (Fig. 8(b)). There are less pits and rupture observed in the inhibited surface. These images clearly show that the inhibition is due to the formation, by adsorption of the organic molecules, of a stable protective

deposit on the copper surface which slows the copper corrosion process in the corrosive solution.

# 4. CONCLUSION

The present work was devoted to the study of the inhibiting action of the *A. Leucotrichus* essential oil (AEO) on the corrosion of copper in an aggressive medium hydrochloric acid 2mol/l, by various methods: Gravimetric, curves of polarization, electrochemical impedance spectroscopy and surface treatment by scanning electron microscopy (SEM). This study was conducted at different concentrations of the inhibitor (500 to 3000 ppm) and at different temperatures (298, 308, 318 and 328 K) to examine the influence of these two parameters on the corrosion rate and the inhibitory efficiency.

Following our investigation, we achieved the following results:

- The addition of AEO has a beneficial effect on the inhibition of corrosion in a 2M hydrochloric acid medium onto copper surface.
- The inhibitory efficacy of AEO rises with rising concentration of the inhibitor and decreases with increasing temperature.
- The electrochemical results clearly indicate that the product AEO has a cathodic effect on copper surface in the hydrochloric acid medium.
- The thermodynamic study showed that the adsorption of this inhibitor on the copper surface is spontaneous and follows the Langmuir adsorption isotherm model, the thermodynamic data of the adsorption process (ΔG<sub>ads</sub> and ΔH<sub>ads</sub>) have calculated from adsorption isotherms.
- Negative values of ΔG<sub>ads</sub> as well as the inhibiting potency which decreases with increasing temperature allow us to classify our inhibitor as physisorbed.
- Observation of the copper surface by SEM showed that the inhibition is due to the formation of an
  adherent and stable deposit which limits the corrosion.
- There is good accordance between the findings achieved by the three approaches.

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## **Declaration of competing interest**

All authors declare no conflict of interests.

# REFERENCES

[1] G. Palanisamy, Corrosion Inhibitors, A. Singh (Eds.), Intech Open, Southwest Petroleum University (2019).

- [2] P. Marcus, and V. Maurice, Fundamental Aspects of Corrosion of Metallic Materials, R.D. Rawlings (Eds.), Eolss, United Kingdom (2009).
- [3] D. Dwivedi, and J. P. Mata, NPJ Mater. Degrad. 3 (2019) 35.
- [4] J. Fu, H. Zang, Y. Wang, S. Li, T. Chen, and X. Lu, Ind. Eng. Chem. Res. 51 (2012) 6377.
- [5] T.W. Quadri, L.O. Olasunkanmi, O.E. Fayemi, M.M. Solomon, and E. E. Ebenso, ACS Omega 2 (2017) 8421.
- [6] K. Hart, and A.O. James, Br. J. Appl. Sci. Technol. 28 (2014) 4052.
- [7] M. Ouknin, J. Cost, and L. Majidi, Chem. Data Collect. 28 (2020)
   DOI: 10.1016/J.CDC.2020.100389.
- [8] A. A. Khadom, J. Chil. Chem. Soc. 59 (2014) 2545.
- [9] I. B. Obot, S. A. Umoren, and N. O. Obi-Egbedi, J. Mater. Environ. Sci. 2 (2011) 60.
- [10] K. Cherrak, F. Benhiba, N. K. Sebbar, E. M. Essassi, M. Taleb, A. Zarrouk, and A. Dafali, Chem. Data Collect. 22 (2019) 100252.
- [11] N.O. Obi-Egbedi, I. B. Obot, and A. O. Eseola, Arab. J. Chem. 7 (2014) 197.
- [12] Y. K. AgrawaL, J. D. Talati, M. D. Shah, M. N. Desai, and N. K. Shah, Corr. Sci. 46 (2004) 633.
- [13] E. M. Sherif, R. M. Erasmus, and J. D. Comins, J. Colloid Interf. Sci. 309 (2007) 470.
- [14] K. F. Khaled, Corros. Sci. 52 (2010) 3225.
- [15] P. Savita, N. Mourya, V. K. Chaubey, and M. M. Singh, Metall. Mater. Trans B. 47 (2015) 47.
- [16] E. M. Sherif, and S. M. Park, Corr. Sci. 48 (2006) 4065.
- [17] E. M. Sherif, Appl. Surf. Sci. 252 (2006) 8615.
- [18] E. M. Sherif, and S. M. Park, Electrochim. Acta. 51 (2006) 6556.
- [19] S. M. Milic, and M. M. Antonijevic, Corr. Sci. 51 (2009) 28.
- [20] M. B. Radovanovic, and M. M. Antonijevic, J. Adhesive Sci. Technol. (2016) 369.
- [21] M. A. Deyab, R. Essehli, and B. El Bali, RSC Advances 5 (2015) 64326.
- [22] K. Dahmani, M. Galai, M. Cherkaoui, A. El hasnaoui, and A. El Hessni, JMES 8 (2017) 1676.
- [23] B. Duran, G. Bereket, and M. Duran, Prog. Org. Coat. 73 (2012) 162.
- [24] A. Fateh, M. Aliofkhazraei, and A.R. Rezvanian, Arab. J. Chem. 13 (2020) 481.
- [25] A. Jmiai, B. El Ibrahimi, A. Tara, R. Oukhrib, S. El Issami, O. Jbara, L. Bazzi, and M. Hilali, Cellulose 24 (2017) 3843.
- [26] M. M. Antonijevic, S. M. Milic, S. M. Serbula, and G. D. Bogdanovic, Electrochim. Acta 50 (2005) 3693.
- [27] A. T. Simonovic, M. B. Petrovic, M. B. Radovanovic, S. M. Milic, and M. M. Antonijevic, Chem. Pap. 68 (2014) 362.
- [28] P. Zhang, Q. Zhu, Q. Su, B. Guo, and S. K. Cheng, Trans Nonferrous Met. Soc. China 26 (2016) 1439.

- [29] M. Manssouri, Y. El Ouadi, M. Znini, J. Costa, A. Bouyanzer, J. M. Desjobert, and L. Majidi, Mater. Environ. Sci. 6 (2015) 631.
- [30] M. Manssouri, M. Znini, A. Ansari, A. Bouyenzer, Z. Faska, and L. Majidi, Der Pharma Chem. 6 (2014) 33.
- [31] A. Boumezzourh, M. Ouknin, A. Bouyanzer, J. Costa, and L. Majidi, Mor. J. Chem. 7 (2019) 141.
- [32] O. Benali, L. Larabi, S. Merah, and Y. Harek., J. Mater. Environ. Sci. 2 (2011) 39.
- [33] I. A. El Haci, C. Bekhechi, F. Atik Bekkara, W. Mazari, M. Gherib, A. Bighelli, J. Casanova, and F. Tomi, Nat. Prod. Commun. 9 (2014) 711.
- [34] Z. Khiati, A. A. Othman, M. Sanchez-Moreno, M. C. Bernard, S. Joiret, E. Sutter, and V. Vivier, Corr. Sci. 53 (2011) 3092.
- [35] D. Tromans, and J.C. SiIva, J. Electrochem. Soc. 143 (1996) 458.
- [36] E. M. Sherif, Int. J. Electrochem. Sci. 7 (2012) 1884.
- [37] L. Larabi, O. Benali, S. M. Mekelleche, and Y. Harek, Appl. Surf. Sci. 253 (2006) 1371.
- [38] D. Zhang, L. I. Gao, and G. Zhou, J. Appl. Electrochem. 35 (2005) 1081.
- [39] D. Q. Zhang, Q. R. Cai, L. X. Gao, and K. Y. Lee, Corr. Sci. 50 (2008) 3615.
- [40] M. Shabani-Nooshabadi, F.S. Hoseiny, and Y. Jafari, Metall. Mater. Trans A. 46 (2015) 293.
- [41] S. Marzorati, L. Verotta, and S.P. Trasatti, Molecules. 24 (2019) 48.
- [42] S. D. Shetty, P. Shetty, and H. V. S. Nayak, Mater. Lett. 61 (2007) 2347.
- [43] S. D. Shetty, and N. Shetty, Int. J. Technol. 5 (2017) 909.
- [44] O. Benali, L. Larabi, and Y. Harek, Saudi Chem. Soc. 14 (2010) 231.
- [45] F. Constantin, J. P. Millet, M. Abrudeanu, and A.G. Plaiasu, Rev. Roum. Chim. 56 (2011) 917.
- [46] L. Larabi O. Benali, and Y. Harek, Electrochim. Acta. 24 (2006) 3376.
- [47] K. Ramya, R. Mohan, K. K. Anupama, and A. Joseph, Mater. Chem. Phys. 149 (2015) 632.
- [48] G. G. Karthik, and M. Sundaravadivelu, J. Adhesive Sci. Technol. 31 (2016) 1072.
- [49] M. Behpour, S. M. Ghoreishi, M. Khayatkashani, and N. Soltani, Corr. Sci. 53 (2011) 2489.
- [50] N. Belarbi, F. Dergal, I. Chikhi, S. Merah, D. Lerari, and K. Bachari, Int. J. Ind. Chem, 9 (2018) 115.
- [51] M. A. Elmorsi, and A. M. Hassanein, Corr. Sci. 41 (1999) 2337.
- [52] L. Majidi, Z. Faska, M. Znini, S. Kharchouf, A. Bouyanzer, and B. Hammouti, J. Mater. Env. Sci. 1 (2010) 219.

- [53] S. Merah, L. Larabi, O. Abderrahim, and Y. Harek, Int. J. Ind. Chem. 8 (2018) 263.
- [54] T. Szauer, and A. Brandt, Electrochim. Acta. 26 (1981) 1257.
- [55] N. Rajae, B. Fouad, R. Youssef, O. Moussa, C. Mohammed, O. Hassan, W. Ismail, and Z. Abdelkader, Anal. Bioanal. Electrochem. 10 (2018) 1375.

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