

## Inhibition of Copper Corrosion in Sulfuric Acid by *Mentha Pulegium L.*

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Received 21/03/2022; accepted 21/05/2022  
<https://doi.org/10.4152/pea.2024420205>

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### Abstract

The application of inhibitors against metals and alloys corrosion in various aggressive environments is an excellent solution. The present study explored Cu corrosion inhibition in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by MP EO, from Western Morocco, using EIS and PDP analyses. GC coupled with MS revealed that MP EO is mainly composed of pulegone (23.38%), isomenthone (20.54%) and l-menthone (9.56%). MP inhibitory behavior was of mixed type. MO EO prevented Cu corrosion in H<sub>2</sub>SO<sub>4</sub>, with an IE(%) that increased with its Ct, at a maximum of 91.0%, with 1 g/L. The Cu surface was studied by SEM coupled with EDS.

**Keywords:** Cu, EDS, EIS, EO, GC, H<sub>2</sub>SO<sub>4</sub>, IE(%), MP, MS and SEM.

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### Introduction\*

Metals are amongst the most widely used materials, particularly in mechanical engineering, transport industry, electronics and construction. However, metals and alloys usefulness is limited by the common problem of corrosion [1, 2]. Corrosion is defined as the deterioration of a metal, due to chemical attack or environmental reaction [3]. Cu is among the materials that are commonly used in heating and cooling systems, due to its excellent thermal conductivity and good mechanical workability [4, 5]. However, scale and corrosion products have a negative effect on heat transfer, and lead to a decrease in the equipment heating efficiency, which requires periodic descaling and cleaning with H<sub>2</sub>SO<sub>4</sub> or HCl pickling solutions [6]. Recently, several studies have examined the possibility of using organic inhibitors mechanisms against metallic corrosion in different acidic media [7, 8, 9]. Considerable efforts have been made to find suitable compounds that inhibit metal corrosion in various aggressive environments [10]. Therefore, metals and alloys protection is of particular interest, and one approach is the use of corrosion inhibitors [11].

Many compounds that are green inhibitors have been investigated for their corrosion prevention potential [12]. All these studies state that organic compounds containing N, S and O in their structures have shown significant IE(%) [13]. These inhibitors retard metals corrosion by being adsorbed onto a metal surface. The adsorption process is influenced by factors such as the inhibitor molecular size and Ct, the substituents nature, T and nature of the test solution [14, 15]. Organic compounds and extracts from plants have been examined for their inhibitory properties, including caffeic acid [16], pennyroyal oil [17], caffeine [18],

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\*The abbreviations and kinetic parameters lists are in page 148.

thyme [19], jojoba oil [20], rosemary oil [21, 22] and eugenol [23]. Polymers, polymeric polyepoxides and epoxy resin [24-28], e.g., TGETBAE and HGTMDAE, are also used as metals corrosion inhibitors [29, 30]. EO are studied for their corrosion IE(%) that is linked to terpenoids, hydrocarbons and S compounds naturally present in different Ct [31, 32]. For the same plants, the EO nature and constituents amount differ according to their origin (climate, soil, altitude), which has a huge impact on their effectiveness. Within this framework, the present study aimed to determine the chromatographic analysis of MP EO, from the region of Zaër (Western Morocco), and to study its IE(%) for Cu corrosion in a 0.5 M H<sub>2</sub>SO<sub>4</sub> medium, by varying two essential parameters: Ct and T.

### **Zaër region**

Zaër region is of trapezoidal shape, located in the heart of Morocco, between the Atlas Mountains and the Atlantic Ocean, at 33° and 34° North latitude and 6° and 7° West longitude, and covers an area of approximately 3.860 Km<sup>2</sup>. [33]. It is bordered to the north by the Rabat region, to the east by the Zemmour region, to the south-west by the Chaouia region and to the south by the Beni Khiran domain. Cherrat, Bou Regreg and Grou rivers set their limits on nearly half of its length. The climate of this region is Mediterranean: mild and humid in winter, and hot and dry in summer; rainfall in the region far exceeds the national average [34].

## **Materials and methods**

### **Plant material**

The genus *Mentha* comprises 25 to 30 species that grow in temperate regions of Eurasia, Australia and South Africa, in the wetlands of plains and mountains up to 2200 meters above sea level [35]. MP, locally called *Fliou*, is also known as pouliot, royal pouliot, flea or chip hunt, and it belongs to the *Lamiaceae* family.

### **MP extraction**

MP was collected from the region of Zaër, Morocco, in April. The extraction of its EO was carried out using a Clevenger apparatus: 230 g MP fresh leaves were introduced into a 2 L flask with distilled water (about 2/3 of the flask), and the mixture was boiled for 4 h. The EO extract (volatile part) was kept in the dark, at 4 °C, for later use.

### **MP EO analyses by GC and MS**

The MP EO volatile part analyses were carried out by GC and MS, at the Centre for Analysis, Expertise, Technology, Transfer and Incubator of the Ibn Tofail University, Kenitra. The analyses conditions were: ionization energy - 70 eV; T - 300 °C; carrier gas - He; He flow rate - 1.70 mL; injection flow rate - 1 µl; injection volume - 1 mL; injection mode - Std Split/splitless; and total time - 40 min. GC was of the type 456 coupled to a MS type EVOQTQ. The column was Rxi - 5 sil MS (30 x 0.25mm ID X 0.25 µm) capillary type, the detector was FID and the software was MS DATA review, with a computerized database (NIST 2014).

### **WE preparation**

The used Cu plate chemical composition (in %) was: 0.019 P, < 0.001 Fe, < 0.001 As, < 0.001 Mn, < 0.002 Sb, < 0.001 Al, 0.009 Sn, 0.003 Ni, 0.015 Pb, < 0.005 Ag, < 0.001 Bi, < 0.001 S, < 0.005 C and Cu (balance). The WE underwent a pre-treatment before each test, which consisted of polishing the electrode surface with different abrasive papers (800, 400, 1200 and 1500 grades), rinsing with distilled water, degreasing in acetone and drying.

### **Corrosive solution preparation**

The corrosive solution was a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, and its pH and T were maintained at 2 and 25 °C, respectively. Solutions of 0.5 M H<sub>2</sub>SO<sub>4</sub> with MP EO were freshly prepared before each experiment.

### **Electrochemical measurements**

Electrochemical measurements were performed using a PGZ100 potentiostat/galvanostat controlled by Volta Master 4 analysis software, in a H<sub>2</sub>SO<sub>4</sub> 0.5 M aqueous solution. The corrosion cell used was equipped with three electrodes: SC electrode (Hg/HgCl<sub>2</sub> in saturated KCl) and Pt wire were used as RE (DHW type) and CE, respectively. All E values given in this work refer to this RE by using a Cu plate as WE (with an exposed surface area of 1 cm<sup>2</sup>). The experiments were carried out after 30 min immersion of Cu in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, without and with MP, at different Ct. The PDP curves were obtained by sweeping the WE E from -1200 to 600 mV, at a SR of 1 mV/s. All electrochemical experiments were performed at a T of 298 K. The Ct range used for MP was from 0.5 to 2 g/L. To evaluate the kinetic corrosion parameters, Stern-Geary equation was used. For this purpose, overall i values were taken as the sum of two contributions, i<sub>a</sub> and i<sub>c</sub>, respectively. For the E range not too far from OCP, both processes followed Tafel's law [36]. Thus, it can be derived from equation (1) that:

$$i = i_a + i_c = i_{\text{corr}} \{ \exp [b_a \times (E - E_{\text{corr}})] - \exp [b_c \times (E - E_{\text{corr}})] \} \quad (1)$$

where  $i_{\text{corr}}$  is in A cm<sup>-2</sup>, and  $\beta_a$  and  $\beta_c$  are in V/dec, at the usual logarithmic scale given by equation (2):

$$\beta = \ln 10 / b = 2.303 / b \quad (2)$$

The corrosion parameters were then evaluated by the NLLS method, applying equation (1), using the Origin software.

The corrosion IE(%) was evaluated from  $i_{\text{corr}}$  values using equation (3):

$$\eta_{\text{pp}} = i_{\text{corr}}^0 - i_{\text{corr}} / i_{\text{corr}}^0 \times 100 \quad (3)$$

where  $i_{\text{corr}}^0$  is  $i_{\text{corr}}$  value without MP. EIS diagrams were produced under the Nyquist plot. The results were then analyzed in terms of equivalent electrical circuit, using Bouckamp's program [37]. IE(%) was also calculated using the following equation (4):

$$\eta_{\text{EIS}} = R_{\text{ct}} - R_{\text{ct}}^0 / R_{\text{ct}} \times 100 \quad (4)$$

where  $R_{\text{ct}}^0$  is  $R_{\text{ct}}$  value without MP.

### **Surface morphology analysis**

To confirm the formation of a layer on the Cu surface immersed in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, for 16 h, with and without MP EO, SEM analysis coupled with EDX microanalysis were carried out at CNRST, Rabat, Morocco.

## **Results and discussion**

### **EO yield**

The extraction with Clevenger apparatus allowed to obtain two fractions: the EO, which is the volatile fraction, and the hydrolate, with a yield of 1.43% from 230 g MP fresh leaves. This content was approximately equal to that obtained by Derwich et al. (1.66%) [38].

### **Product analysis by GC/MS coupling**

Through GC/MS analysis, it was possible to identify a total of 31 compounds for MP (listed in Table 1).

**Table 1:** MP EO composition.

N	Retention time (min)	Percentage (%)	Compound name
1	8.060	0.61	E-3-Hexenol
2	12.992	0.29	3-Methylcyclohexanone
3	13.787	0.11	(-)- $\beta$ -Pinene
4	14.193	0.14	3-Octenol
5	14.582	0.44	Octan-3-ol
6	15.332	3.98	(+)-Limonene
7	15.364	0.45	Eucalyptol
8	18.114	20.54	Isomenthone
9	18.178	9.56	l-Menthone
10	18.565	5.51	Isopulegone
11	18.826	2.24	Menthol
12	18.983	1.9	3-hydroxy-4,4-dimethyldihydrofuran-2-one
13	19.035	0.66	(E)-2, 2, 5,5-tetramethyl-3-hexene
14	19.378	23.38	Pulegone
15	19.431	2.12	1-Dodecyne
16	19.466	3.08	(4Z)-2-isopropylhexa-1,4-diene
17	19.545	3.85	Cyclohexanone, 2-isopropylideno-5-methyl
18	19.619	1.37	(1R)-1-methoxymyodesertan
19	19.676	3.75	(Z)-6-methyl-5-methylene-2-heptene
20	19.704	2.59	Spiro[2.5]octane
21	19.766	3.01	2-Cyclohexyloxirane
22	20.146	0.14	Carbonic acid, (1R)-(-)-menthyldecyl ester
23	20.163	0.15	(S)-(+)-cis-Isopiperitenone
24	20.280	0.88	(7-Hydroxy-3,3-dimethyl-4-oxo-7-vinylbicyclo[3.2.0] hept-1-yl)acetaldehyde
25	20.325	0.80	Dihydroedulan
26	20.449	1.32	(-)-Neomenthylacetate
27	20.474	1.02	2-Isopropyl-3-methylcyclohexyl acetate
28	20.501	1.59	l-Menthol acetate
29	20.919	3.16	Piperitenone
30	22.334	1.19	Humulene
31	24.506	0.17	$\beta$ -Acoradienol

MP EO extracted using Clevenger apparatus has pulegone as its main constituent, with a content of 23.38%, and also: (-)-beta-pinene (0.11%), 3-octenol (0.14%), octan-3-ol (0.44%), (+)-limonene (3.98%), eucalyptol (0.45%), isomenthone (20.54%), l-menthone (9.56%), isopulegone (5.51%), menthol (2.24%), piperitenone (3.16%), l-menthol acetate (1.59%) and humulene (1.19%).

These compounds are considered to be good corrosion inhibitors, due to the presence of pulegone, as found in other work [39]. These results are compatible with most of the work already carried out in Morocco, which confirms that Moroccan MP EO is rich in pulegone [40]. The same is true for MP collected throughout the world, which shows that it belongs to the pulegonechemo type [41]. Several works have studied MP EO inhibition mechanism [42] but, to our knowledge, not against Cu corrosion in H<sub>2</sub>SO<sub>4</sub>.

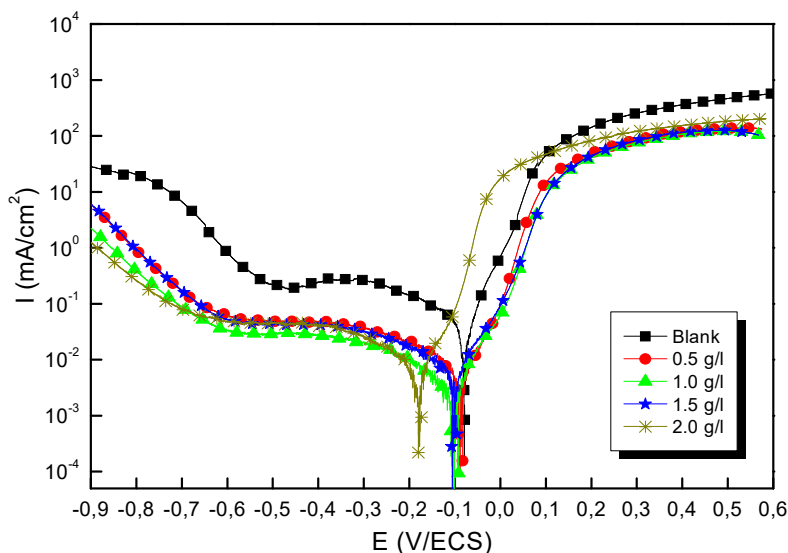
### **PDP**

#### *Ct effect*

Fig. 1 shows a set of polarization curves for the Cu electrode immersed in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without and with MP EO, at different Ct. Each polarization curve is

formed of two half curves, one representing anodic (Cu dissolution) and another cathodic domains (O reduction). The involved redox reactions are:

- Reduction reaction:  $O_2 + 4 H^+ + 4e^- \longrightarrow 2H_2O$
- Oxidation reaction:  $Cu \longrightarrow Cu^{2+} + 2e^-$



**Figure 1:** Polarization curves of Cu in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with MP EO.

Various studies have confirmed that, although MP EO has shown high IE(%) against metals corrosion, it is dependent on the extract Ct [43, 44]. For this study, by comparing the polarization curves, without and with MP EO, higher inhibitor Ct shifted E value in the negative direction, and caused a slight decrease in  $i_a$  and  $i_c$  densities. However, MP EO corrosion IE(%) was significant at a Ct of 1.0 g/L, reaching the maximum value of 91.0%. Table 2 shows some examples in the literature of MP as a green corrosion inhibitor:

**Table 2:** Examples of MP used a corrosion inhibitor.

EO inhibitor	Medium	Type of metal	Maximum IE(%)	Ref
MP	1 M HCl	MS	90% at 1 g/L	[45]
	0.5 M H <sub>2</sub> SO <sub>4</sub>	MS	89.7% at 4g/ L	[46]
	2 M H <sub>3</sub> PO <sub>4</sub>	Aluminum	79% at 1800 ppm	[47]
	0.1 M Na <sub>2</sub> CO <sub>3</sub>	Aluminum	94.16% at 800 ppm	[48]
	0.5 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Tinplate	80% at 4 g/ L <sup>-1</sup>	[49]

Kinetic parameters such as  $E_{corr}$ ,  $i_{corr}$ ,  $\beta_c$ ,  $\beta_a$  and IE(%) are listed in Table 3.

In the literature, it has been reported that, if the displacement in  $E_{corr}$  is  $> 85$  mV, the inhibitor can be considered cathodic or anodic, and if it is  $< 85$  mV, it can be considered of the mixed type [50].

In our study, according to Table 3, we note that MP EO addition reduced  $i_{corr}$  from 29 to 2.4  $\mu\text{A}/\text{cm}^2$ . Thus, Cu resisted corrosion in the inhibitor presence. This may be due to MP EO adsorption onto the metal/acid interface. Nevertheless, the decrease in MP EO  $i_{corr}$ , compared to the blank 0.5 M H<sub>2</sub>SO<sub>4</sub>, for the anodic and

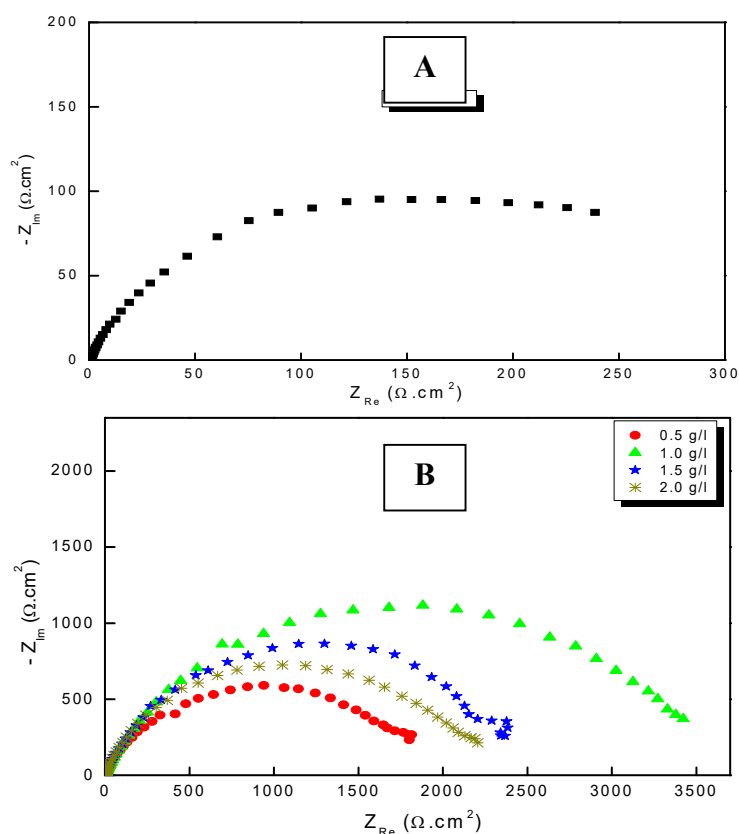
cathodic sites, may indicate a mixed type of corrosion inhibition. Moreover, the displacement of  $E_{\text{corr}} < 85$  mV confirms the behavior of a mixed type inhibitor.

**Table 3:** Electrochemical parameters of the stationary polarization curve of Cu in a  $\text{H}_2\text{SO}_4$  0.5 M medium.

Inhibitor	Ct g/L	$E_{\text{corr}}$ (mV/ECS)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Tafel slopes (mV/dec $^{-1}$ )		IE(%)
				$-\beta_c$	$\beta_a$	
Blank	--	-79	29.0	204	59	-
	0.5	-80	5.0	189	56	82.7
MP	1.0	-86	2.6	183	52	91.0
	1.5	-89	3.7	185	53	87.2
	2.0	-169	4.3	187	54	85.2

### EIS

In order to better understand the phenomenon occurred on the metal/solution interface, we have drawn the impedance diagram shown in Fig. 2.



**Figure 2:** Nyquist plots for Cu in a 0.5 M  $\text{H}_2\text{SO}_4$  solution: (A) without; and (B) with MP EO various Ct, at 298 K.

Through comparison of the uninhibited 0.5 M  $\text{H}_2\text{SO}_4$  solution with the inhibited one, we notice that the display of the Cu impedance in the medium with MP EO changed considerably in shape and size (Fig. 2). The impedance data are simulated using the equivalent circuit illustrated in Fig. 4, for the electrode immersion in an  $\text{H}_2\text{SO}_4$  solution containing MP EO, during only 60 min. The inhibitor caused

changes in impedance behavior. The increase in  $R_{ct}$  values was due to the development of a protective film at the metal-solution interface [51].  $R_p$  diameter obviously increased, from  $350/\Omega\text{cm}^2$ , without MP EO, to over  $3636 \Omega/\text{cm}^2$ , with it (Table 4).

**Table 4:** Electrochemical parameters of the Cu electrochemical impedance curve.

Inhibitor	Ct g/L	$R_s$ $\Omega/\text{cm}^2$	$Q_f$ $\mu\text{F}/\text{cm}^2$	$n_f$	$R_f$ $\Omega/\text{cm}^2$	$Q_{ct}$ $\mu\text{F}/\text{cm}^2$	$n_{ct}$	$R_{ct}$ $\Omega/\text{cm}^2$	$R_p$ $\Omega/\text{cm}^2$	IE%
Blank	--	$0.7\pm 0.2$	-	-	-	$475\pm 9.1$	$0.72\pm 0.007$	$350\pm 5.1$	350	-
	0.5	$2.3\pm 0.9$	$35.9\pm 4.8$	$0.903\pm 0.007$	$94\pm 7.1$	$150\pm 4.4$	$0.569\pm 0.008$	$1892\pm 7.1$	1986.0	82.4
Inhibitor	1.0	$2.3\pm 1.0$	$5.7\pm 1.8$	$0.997\pm 0.007$	$12.8\pm 1.6$	$81.6\pm 2.1$	$0.673\pm 0.008$	$3624\pm 14.2$	3636.8	90.4
	1.5	$1.8\pm 1.0$	$9.9\pm 1.7$	$0.998\pm 0.007$	$18.7\pm 1.4$	$96.4\pm 3.8$	$0.673\pm 0.008$	$2526\pm 73.8$	2544.7	86.2
	2.0	$1.8\pm 1.0$	$17.4\pm 1.9$	$0.952\pm 0.007$	$38.2\pm 5.4$	$106.2\pm 5.6$	$0.669\pm 0.008$	$2264\pm 12.5$	2302.2	84.8

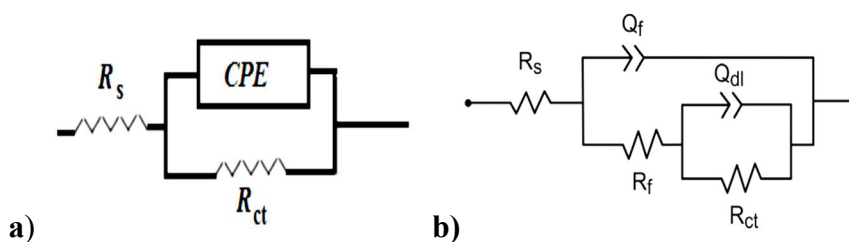
From the shape of the capacitive loops, we see that the corrosion process was controlled by a diffusion mechanism. This was confirmed by [52, 53]. The diameter of these capacitive loops increased progressively with higher MP EO Ct, which indicates a strengthening of the inhibitory film. The electrochemical parameters of these diagrams are shown in Table 4.

In Fig. 3, the condenser was replaced by a CPE, which indicated the presence of a dissimilar frequency response. CPE impedance is defined as follows [54]:

$$Z_{CPE}(\omega) = Q^{-1}(j\omega)^{-n}$$

where  $Q$  is a constant in  $\Omega/\text{cm}^2$  in  $\text{s}^n$ ,  $\omega$  is the angular frequency in rad/s and  $n$  is CPE exponent, with  $-1 < n < 1$ .

CPE can represent an inductance, a Warburg impedance, a pure capacitance, or a resistance, with  $n = -1, 0.5, 0$  and  $1$ , respectively. The smaller the  $n$  value, the higher the surface roughness [55].

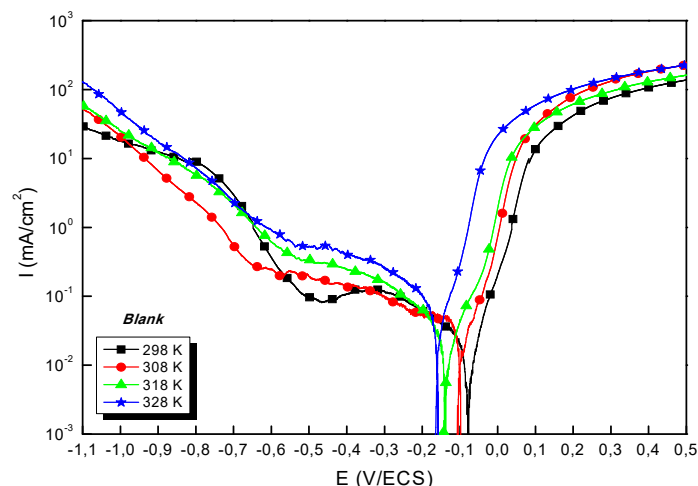


**Figure 3:** Equivalent circuits for Cu EIS used to model Cu/solution interface without (a) and (b) with MP EO.

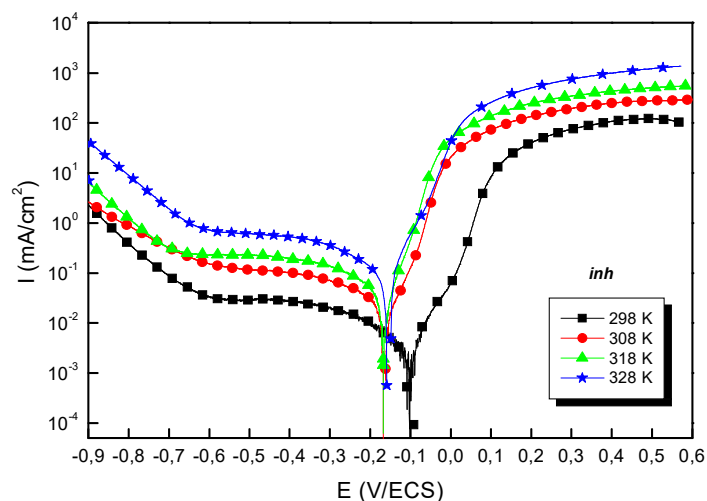
#### *T effect and thermodynamic parameters*

The  $T$  of the corrosive environment is one of the factors that can modify the behavior of materials in a given corrosive environment, as well as the IE(%) of a compound. In general, as  $T$  increases, changes in the inhibitor action occur.

Due to the importance of this factor, trace tests of the polarization curves for the  $0.5 \text{ M H}_2\text{SO}_4/\text{Cu}$  interface with and without MP EO, at different  $T$ , were performed. They are shown in Figs. 4 and 5.



**Figure 4:** PDP curve for Cu in 0.5 M H<sub>2</sub>SO<sub>4</sub> without MP EO, at different T.



**Figure 5:** PDP curve for Cu in 0.5M H<sub>2</sub>SO<sub>4</sub> with MP EO, at different T.

The electrochemical parameters from these diagrams are shown in Table 5.

**Table 5:** Electrochemical parameters from the stationary polarization curves of Cu without and with MP, at different T.

Compound	T (K)	-E <sub>corr</sub> (mV/ECS)	i <sub>corr</sub> (μA/cm <sup>2</sup> )	-β <sub>c</sub> (mV)	β <sub>a</sub> (mV)	IE(%)
Blank	298	79	29.0	204	59	-
	308	105	35.0	188	64	-
	318	142	56.0	164	77	-
	328	166	77.0	152	52	-
1.0 g/L MP	298	86	2.6	183	52	91.0
	308	164	3.8	171	56	89.1
	318	166	7.2	152	66	87.2
	328	159	11.8	143	70	84.6

Theoretically, higher T increase PDP curves *i* value and decrease IE(%) [56]. This is illustrated more clearly, in Table 4, by *i*<sub>corr</sub> variation with T: *i* varied from 29.0 to 77.0 μA/cm<sup>2</sup>, at 298 and 328 K, respectively. CR dependence on T can be expressed by Arrhenius equation:

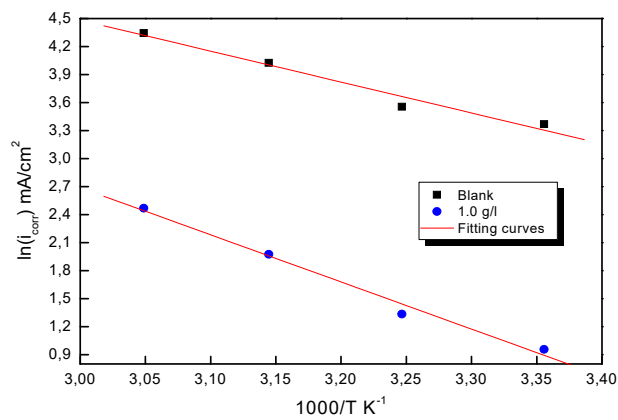


$$i_{corr} = (-E_a/RT) \tag{5}$$

where A is the frequency factor and R is universal gas constant (8.314 J/mol<sup>-1</sup>/K<sup>-1</sup>). The Arrhenius plot that obtained Ln  $i_{corr}$  as a function of 1000/T is shown in Fig. 6, and is compared with that of Cu in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without EO. The experimental curve obtained for MP EO corresponded approximately to a straight line, and anodic E value was determined from the slope of this line. In addition, other kinetic parameters, such as  $\Delta H_{ads}$  and  $\Delta S_{ads}$ , were obtained from the following transition state equation:

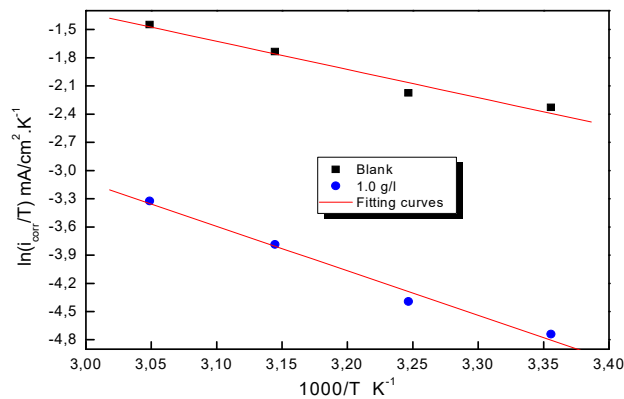
$$\ln\left(\frac{i_{corr}}{T}\right) = \left(\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{R}\right) - \frac{\Delta H_a}{RT}$$

where h is Plank's constant and N is Avogadro's number.



**Figure 6:** Arrhenius plots for Cu in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with MP EO.

Ln ( $i_{corr}/T$ ) variation as a function of 1000/T in 0.5 M H<sub>2</sub>SO<sub>4</sub> gave a straight line, as shown in Fig. 7, with a slope of  $-\Delta H_a/R$ . The intersection with the x-axis is  $\ln(R/Nh) + (\Delta H_a/R)$ .



**Figure 7:** Arrhenius diagrams of Ln ( $i_{corr}/T$ ) versus 1000/T for Cu in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with MP EO.

Adjustment of the curve (Fig. 7) with a straight line gave a value of 41.9 kJ/mol<sup>-1</sup> for the corrosion process  $E_a$  with MP EO. This value is much higher than that for

Cu without MP ( $27.50 \text{ kJ mol}^{-1}$ ), which explains why the variations in  $i_{\text{corr}}$  were more pronounced with the inhibitor (Table 6).

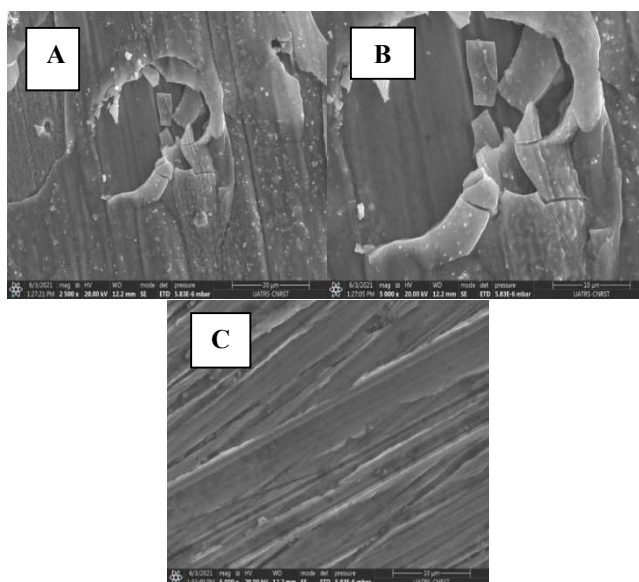
**Table 6:** Values of  $E_a$ ,  $\Delta H_a$  and  $\Delta S_a$  kinetic parameters for Cu in 0.5 M  $\text{H}_2\text{SO}_4$  without and with MP EO.

Compound	$E_a$ ( $\text{kJ/mol}^{-1}$ )	$\Delta H_a$ ( $\text{kJ/mol}^{-1}$ )	$\Delta S_a$ ( $\text{J/mol}^{-1}/\text{k}^{-1}$ )
Blank	27.50	25.00	-134.0
1.0 g/L MP	41.9	39.3	-105.3

The increase in anodic  $E_{\text{corr}}$ , in MP EO presence, associated with a decrease in IE(%), with higher T, is frequently understood as being due to the formation of an adsorption film of a physical nature, i.e. involving electrostatic interactions with the metal surface, according to Popova et al. [57]. The results of the present work suggested a predominant physisorption inhibition. However,  $\Delta H_a$  positive signs reflect Cu dissolution process endothermic nature. Indeed, higher  $\Delta H_a$  in MP EO presence corresponds to a decrease in the metal dissolution.

### Surface analysis

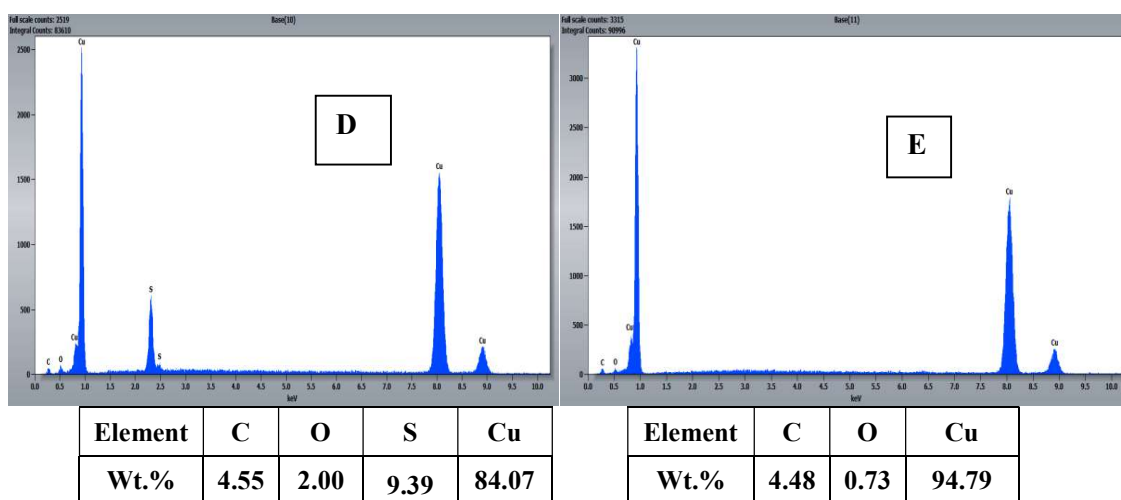
To confirm the results obtained by electrochemical measurements, the surface morphology of Cu samples with and without MP EO, after 16 h of immersion, was studied by SEM (Fig. 8), and the chemical composition was obtained by EDX microanalysis (Fig 9).



**Figure 8:** SEM images of the Cu surface immersed in 0.5 M  $\text{H}_2\text{SO}_4$  solutions, for 16 h, at 298 K: **A** and **B**- without inhibitor; and **C** with inhibitor.

The results show that: the Cu coupon control sample (Fig. 8 A and B), immersed in 0.5 M  $\text{H}_2\text{SO}_4$  without MP EO, was very damaged, since it had a very rough surface, with corrosion products and cracks, due to the attack by the aggressive solution, showing pronounced dissolution; MP EO addition caused a decrease in

Cu degree of corrosion, with cracks disappearance and a regular and smoother morphology (Fig. 8 C), which indicates the formation of a protective film on the metal surface; EDX microanalysis (Fig. 9) shows a decrease in O percentage, and the disappearance of S peak after MP EO addition. Since S and O corrode Cu, their decrease explains the metal surface regularity during the treatment with MP EO. This was due to the formation of a film on the Cu surface by the inhibitor molecules, which protected it from the corrosive attack; therefore, SEM images and EDX microanalysis results are consistent with those of PDP and EIS tests.



**Figure 9:** EDX spectra for the Cu surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions, for 16 h, at 298 K: **D**- without inhibitor; and **E**- with inhibitor.

## Conclusion

This work was part of a long and important line of research aimed at valorizing natural plant resources, in particular, the aromatic and medicinal plants of Morocco. In this context, we have chosen to study MP from the Zaër region, based on traditional uses by the Moroccan population. At the end of this study, we can deduce the following conclusions: GC/MS analyses of MP EO allowed to determine its chemical composition, and pulegone was determined as the major compound; MP EO acted as Cu corrosion inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub>; MP EO IE(%) reached 91.0% at a Ct of 1.0 g/L; MP EO acted as a mixed inhibitor, and its IE(%) increased with higher T.

## Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Authors' contributions

**S. Rached:** wrote the paper. **K. Mzioud:** collected the data. **A. Habsaoui:** conceived and designed the analysis. **M. Galai:** conceived and designed the analysis. **K. Dahmani:** collected the data. **M. Ouakki:** performed the analysis. **S. EL Fartah:** collected the data. **N. Dkhireche:** wrote the paper. **M. Ebn Touhami:** inserted data or analysis tools.

### **Abbreviations**

$\beta_a$ : anodic Tafel slope constant  
 $\beta_c$ : cathodic Tafel slope constant  
**Ct**: concentration  
**CE**: counter electrode  
**CPE**: constant phase element  
**CR**: corrosion rate  
**E**: potential  
 $E_{\text{corr}}$ : corrosion potential  
**EDS**: energy dispersive X-ray  
**EIS**: electrochemical impedance spectroscopy  
**EO**: essential oil  
**GC**: gas chromatography  
**H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>**: oxalic acid  
**H<sub>2</sub>SO<sub>4</sub>**: sulphuric acid  
**H<sub>3</sub>PO<sub>4</sub>**: phosphoric acid  
**HCl**: hydrochloric acid  
**HGTMDAE**: hexaglycidyltrimethylenedianiline of ethylene  
**i**: current density  
 $i_a$ : anodic current  
 $i_c$ : cathodic current  
 $i_{\text{corr}}$ : corrosion current density  
**IE(%)**: inhibition efficiency  
**MP**: Mentha pulegium  
**MS**: mass spectrometry  
**Na<sub>2</sub>CO<sub>3</sub>**: sodium carbonate  
**NLLS**: non-linear least square  
**OCP**: open-circuit potential  
**PDP**: potentiodynamic polarization  
**R<sub>ct</sub>**: charge transfer resistance  
**Redox**: reduction-oxidation reactions  
**RE**: reference electrode  
**R<sub>p</sub>**: polarization resistance  
**SC**: saturated calomel  
**SEM**: scanning electron microscopy  
**SR**: scan rate  
**T**: temperature  
**TGETBAE**: triglycidyl ether tribisphenol A of ethylene  
**WE**: working electrode

### **Kinetic parameters abbreviations**

$\Delta H_a$ : activation enthalpy  
 $\Delta S_a$ : activation entropy  
 $\Delta H_{\text{ads}}$ : enthalpy of adsorption  
 $\Delta S_{\text{ads}}$ : entropy of adsorption  
 $E_a$ : activation energy

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