

## Chemical composition of essential oil and antioxidant and anti-corrosion activity of extract and essential oil of Pennyroyal Mint (*Mentha pulegium*, MP)

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### Abstract

View the growing success of natural products as an alternative to synthetic chemicals. The purpose of this study was to contribute to the valorization of leaves of *Mentha pulegium* by determining the chemical composition of its essential oil and evaluate in vitro the antioxidant and the anticorrosive activities of its aqueous extract and essential oil. The essential oil revealed 1,8-Cineole (31.9%) followed by piperitone (15.6%), Limonene (14.6%) and  $\beta$ -Pinene (4.8%) as the main constituents. The antioxidant activity of aqueous extract was evaluated by the method of DPPH radical scavenging. The extract and the essential oil of *M. pulegium* were tested as corrosion inhibitors of mild steel in 0.5 M  $H_2SO_4$  using weight loss measurements and electrochemical methods. The aqueous extract exhibited a moderate antioxidant activity compared to acid ascorbic and the  $IC_{50}$  value was 36,62  $\mu g/mL$ . The obtained results have showed that the inhibition efficiency increases with increasing inhibitor concentration to attain 90.3 % at 2 g/L of MPE and 87.3 % at 4g.L<sup>-1</sup> of MPO at 303 K. Finally, extracts and essential oil of *M. pulegium* from Mediterranean origin have numerous potential as a substitute to chemical additives for the food industry.

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Received 11 Nov 2016,

Revised 15 Janv 2017,

Accepted 20 Feb 2017

**Keywords:** *M. pulegium*, adsorption, corrosion, inhibition, carbon steel, essential oil, extract, sulfuric acid.

## 1. Introduction

The family of Lamiaceae or Labiatae comprises of about 230 genera and 7100 species worldwide [1]. Major genera belonging to Lamiaceae family are commonly known as producers of essential oils such as *M. pulegium* L, *Salvia*, and *Sideritis*. *M. pulegium* is native to North Africa, Europe and Asia and is naturalized in America and thrives in Western, Iran, Arab countries and Ethiopia [2]. Essential oil and dry aerial parts of *M. pulegium* are considered of high importance in medicine and they have been traditionally used in medicine for treatment of disorders, colds, gastronomy (culinary herb), aromatherapy and cosmetics [3, 4]. It is also known for its antispasmodic, carminative, antiseptic, anti-inflammatory [5], antioxidant [6-8], and antimicrobial properties [9, 8]. Recently the interest on natural antioxidants has increased compared to previous years. Scientific researches have been focused to extract, identify and quantify these compounds from several natural substances including medicinal and food plants [10-12]. Another advantage is also brought to the use of these plants as a source of corrosion inhibitors against Iron and alloys. They are the most consumed materials and extensively used for constructional, industrial and numerous engineering applications [13]. However, these materials in question are susceptible to corrosion, especially in acid media. Mineral Acid solutions are frequently used in industry and their main important fields in their broad spectrum of applications are acid pickling, industrial cleaning, acid descaling, oil-well acidizing and petrochemical processes [14-16]. Nevertheless, most of acid media cause the detriment of materials, considerable economic losses [17], and generally lead to serious metallic corrosion [15]. To overcome this unavoidable problem, inhibitors are generally used [18].

In the last few years, many synthetic organic compounds have shown excellent anticorrosive activity in order to protect metallic materials against deterioration due to corrosion, especially in aggressive media. The majority of them are significantly toxic to both human beings and environment [19]. The toxicity may manifest either during the synthesis of the compound or during its applications.

The development of non-toxic and harmless inhibitors is measured more important and advantageous from the standpoint of safety. Actually green inhibitors displaying substantially improved environmental properties will be the most widely used inhibitors in the future [20-29]. In the past two decades, the research in the field of “green” corrosion inhibitors has been addressed toward the goal of using cheap and effective molecules at low or “zero” environmental impact [30].

## 2. Experimental Section

### 2.3. *Plant collection*

The aerial parts of *M. pulegium* were harvested in May from the area of Al Hoceima National Park (Morocco) and located at 35°14'04.6"N latitude and 3°58'45.0"W longitude. A voucher specimen was deposited in the Herbarium of Faculty of Sciences, Oujda, Morocco. The dried plant material was stored in the laboratory at room temperature (298 K) and in the shade before the extraction.

### 2.4. *Solutions preparation*

#### • *Hydrodistillation apparatus and procedure*

The dried leaves of *M. pulegium* were water distilled (3h) using a Clevenger-type apparatus according to the method recommended in the European Pharmacopoeia [31]. The essential oil yields were 0.74% (w/w) according to the dry material. The essential oil obtained was dried under anhydrous sodium sulfate and stored in sealed glass vials at 4-5 °C in the darkness prior to analysis. Stock plant extract was prepared by an aqueous maceration.

## 2.5. Determination of total phenolic content of extract

The determination of total phenolics of aqueous extract was carried out with the Folin-Ciocalteu colorimetric method [32]. Briefly 0.2 ml of the extract was mixed with 1 ml of a reagent Folin Ciocalteu 10% (v/v). After 4 min of incubation, 0.8 mL of sodium carbonate (75 g/L) was added to mixture. After 30 min of reaction at room temperature, the absorbance was measured at 765 nm. The concentration of total polyphenols is calculated from the equation regression established with the standard gallic acid and expressed as gallic acid equivalent per gram of powder (GAE/g powder) ( $y=0,0052.x+0,0258$ ,  $r^2=0,9957$ ).

## 2.6. Determination of total flavonoids content of extract

The method of aluminum trichloride  $\text{AlCl}_3$  [33] was used to quantify the flavonoids content of extract. In brief, 1 ml of each sample and standard (dissolved in ethanol) was added to an equal volume of a solution of  $\text{AlCl}_3$  (2% in ethanol). The mixture was stirred vigorously and the absorbance at 430nm was read after 10 minutes of incubation. Total flavonoids content were expressed as quercetin equivalent per gram of powder (QE/g powder) ( $y=0,0344.x+0,0088$ ,  $r^2=0,991$ ).

## 2.7. Determination of total flavonols content of extract

The slightly modified method of aluminum trichloride  $\text{AlCl}_3$  [34] was used to quantify the content of flavonols for the studied extract. In a test tube are introduced: 2.8 ml of distilled water, 0.1 ml of  $\text{AlCl}_3$ , 0.1 ml of  $\text{CH}_3\text{CO}_2\text{K}$  (1 M), 0.5 ml of the extract, the mixture is stirred vigorously, and then incubated in the shade at room temperature for 30 minutes. Absorbance is read at 415 nm. Quantification of flavonols is based on a calibration curve obtained by a standard flavonoid quercetin ( $y=0,008.x-0,016$ ,  $r^2=0,998$ ). The flavonol content is expressed in milligrams quercetin equivalent per gram dry weight of the plant (EQ mg / g Ps).

## 2.8. DPPH radical scavenging activity

The radical scavenging activity of aqueous extract against the stable 1,1-diphenyl-2-picryl hydrazyl radical (DPPH) was determined spectrophotometrically [35]. Briefly 0.1 ml of aqueous extract (tested at concentrations ranging from 5 to 100  $\mu\text{g}$  / ml) was added to an ethanol solution (1.9 ml) of the DPPH radical. The mixture was stirred vigorously and allowed to stand at room temperature for 30 min in the dark. The scavenging activity DPPH radical was expressed as percentage inhibition by the following formula. Where,  $A_{\text{sample}}$  is the absorbance of the solution containing the sample at 515 nm, and  $A_{\text{blank}}$  is the absorbance of the DPPH solution. The  $\text{IC}_{50}$  values were calculated as the concentration of extract causing a 50% inhibition of DPPH radical.

$$\left[ (A_{\text{blank}} - A_{\text{sample}}) / A_{\text{blank}} \right] \times 100$$

## 2.9. Weight loss measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat cooling condenser. Sheets with dimensions  $2.5 \times 2 \times 0.5 \text{ cm}^3$  were immersed in 0.5 M of sulfuric acid containing different concentrations of inhibitors at constant temperatures 35, 40, 60, 70°C and  $80 \pm 0.1$  °C using a thermostat for 6 h. The solution volume was 50 ml.

**Table 1.** Chemical composition of mild steel

C	Si	P	Al	Mn	S	Fe
0.21%	0.38%	0.09%	0.01%	0.05%	0.05%	balance

The experiments were performed with mild steel with the following composition table 1. Samples were mechanically polished with emery paper up to 1200 grade, degreased in acetone and then washed with double-distilled water.

### 2.10. Polarization and EIS measurements

Electrochemical measurements were carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. The corrosion cell used had three electrodes. A saturated calomel electrode (SCE) was used as reference, platinum electrode as auxiliary electrode with surface area of 1 cm<sup>2</sup> and the working electrode (WE) was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to establish a steady state open circuit potential ( $E_{\text{corr}}$ ). The test solution was thermostatically controlled at 308 K in air atmosphere without bubbling. All potentials were measured against SCE. Potentiodynamic polarization curves were plotted at a polarization scan rate of 1 mV/s. The polarization curves are obtained in the potential range from -800 mV to -200 mV at 308 K. The EIS experiments were conducted in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. Before recording the curves the test solution is de-aerated in magnetically stirred for 30 min in the cell with nitrogen.

## 3. Results and discussion

### 3.3. Pennyroyal oil analysis

Qualitative and quantitative analyses essential oils were done using GC/MS analyses. The composition of essential oil of Pennyroyal was shown in the Table 1. The analysis of essential oil from *M. pulegium* was carried out by CG/SM.

**Table 2:** chemical constituents of Pennyroyal oil (%)

Composés	IL	Ir /apol	Ir /pol	% apol
a-Thujene	932	923	1022	0,5
$\alpha$ -Pinene	936	931	1022	2,0
Camphene	950	944	1066	0,3
Sabinene	973	967	1120	3,2
$\beta$ -Pinene	978	972	1112	4,8
Myrcene	987	982	1157	1,3
Limonene	1025	1023	1203	14,6
1,8-Cineole	1024	1023	1210	31,9
g-Terpinene	1051	1050	1229	0,4
Terpinolene	1082	1080	1245	0,1
Menthone	1136	1134	1454	1,2
d-Terpineol	1155	1149	1590	1,5
neo-Menthol	1156	1152	1632	2,0
Terpinen-4-ol	1164	1163	1586	0,8
$\alpha$ -Terpineol	1176	1175	1682	3,1
Pulegone	1215	1220	1632	2,2
piperitone	1226	1240	1715	15,6
Piperitenone oxyde	1335	1346	1934	4,1
trans-Caryophyllene	1421	1418	1561	3,0
$\gamma$ -Muurolene	1474	1476	1649	2,7
Bicyclogermacrene	1494	1491	1700	2,6
$\delta$ -Cadinene	1520	1514	1746	0,2
			TOTAL	98.1

### 3.4. Determination of total phenolic content (TPC), total flavonoids (TF) and flavonols

Recently several studies have shown that phenolic compounds such as flavonoids, flavonols are considered mainly factors involved in the antioxidant capacity of plants and other biological activities of plants, such as anti-bacterial activity [38]. Thus, the TPC, TF and flavonols of the plant extract were evaluated and listed in Table 3. The aqueous extract of *M. pulegium* was revealed to be very rich in phenol content ( $188.70 \pm 2,70$ ) mg GAE/g. Also D.Stagos et al., 2012 [39] found a similar value 188 mg GAE/g powder. The flavonoids and flavonols content in the aqueous extract of *M. pulegium* was found as ( $10.72 \pm 0.16$  and  $20,73 \pm 1.06$ ) mg QE/g, respectively.

**Table 3:** Phenolic compounds of aqueous extract of *M. pulegium*

Extrait	TPC <sup>(a)</sup>	TF <sup>(b)</sup>	Flavonols <sup>(b)</sup>
EAqMP	$188,70 \pm 2,72$	$10,72 \pm 0,16$	$20,37 \pm 1,06$

All the values are mean  $\pm$  SD; SD: standard deviation <sup>(a)</sup> (mg GAE/g powder) and <sup>(b)</sup> (mg QE/g powder).

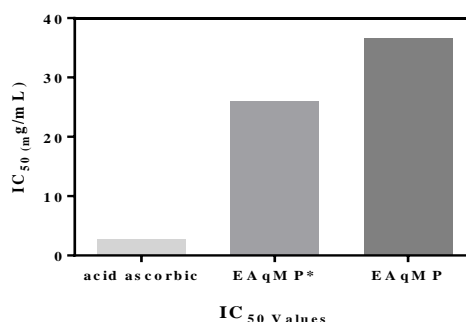
### 3.5. Scavenging activity of DPPH radical

Compounds of plant extracts exhibit a significant source of compounds which can provide an electron or hydrogen radical to stabilize the stable radical DPPH in solution. In this case, the free radical-scavenging activity has been studied in order to evaluate the capacity of the extract by measuring the decrease in absorbance induced by plant antioxidants [40]. In the present work, the aqueous extract IC<sub>50</sub> value was 13 times higher than that of acid ascorbic as shown in Table 4.

**Table 4:** DPPH radical scavenging activity of aqueous extract of *M. pulegium*

Compounds	IC <sub>50</sub> (μg/mL)	
EAqMP	36,62	present study
EAqMP	26,00	D.Stagos et al., 2012
Acid Ascorbic	2,82	present study

Previous study on the antioxidant activity, measuring by DPPH assay, showed an IC<sub>50</sub> 9 times lower than that of acid ascorbic [39]. Finally we can conclude that extract aqueous of *M. pulegium* exhibit a moderate antioxidant abilities to reduce DPPH radicals.



### 3.6. Effect of concentration

#### 3.6.1. Weight loss, corrosion rates and inhibition efficiency

Il gravimetric measurements of mild steel were investigated in aerated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 308 K in the absence and the presence of various concentrations of MPE and MPO at 6 h of immersion. The inhibition efficiency (Ew%) was determined by using the following equation:

$$E_w \% = \frac{W_{\text{corr}} - W'_{\text{corr}}}{W_{\text{corr}}} \times 100 \quad (1)$$

where  $W_{\text{corr}}$  and  $W'_{\text{corr}}$  are the corrosion rate of carbon steel in the absence and the presence of inhibitor, respectively. Table 5 summarizes the gravimetric trends of the carbon steel immersed in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence and the presence of the inhibitors at various concentrations.

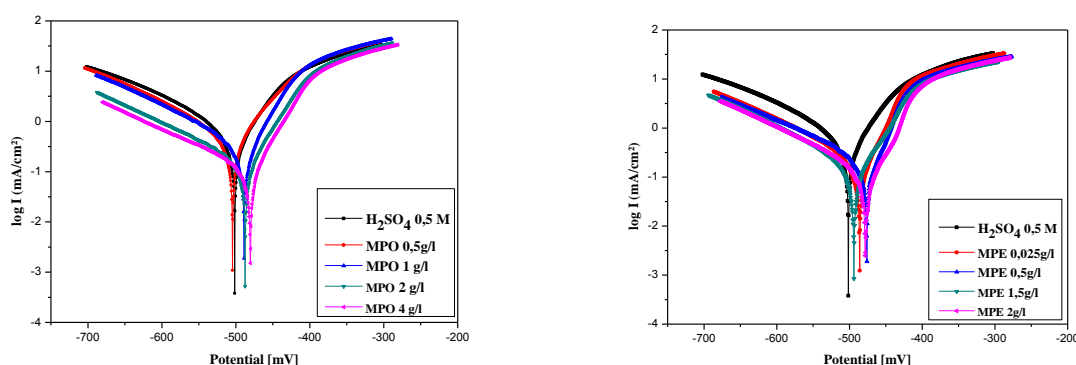
**Table 5.** Gravimetric results of mild steel in acid solutions 0.5 M  $\text{H}_2\text{SO}_4$  at different concentration of MPE & MPO (308 K & 6 h).

Compounds	Concentrations (g/L)	W ( $\text{mg.cm}^{-2}.\text{h}^{-1}$ )	E %
Blank	1M	0.520	-
	0.5	0.138	45.9
Mentha pulegium	1	0.348	57.7
Oil	2	0.570	74.1
	4	0.792	<b>89.7</b>
	0.25	0.260	50.0
Mentha pulegium	0.5	0.197	62.1
Extract	1	0.110	78.8
	2	0.050	<b>90.3</b>

It can be seen from the table that the inhibition efficiency ( $E_w\%$ ) increases to attain 90.3 % and 89.7% for MPE and MPO at 2g/L and 4g/L respectively, and in the turn the corrosion rate decreases with the increase of concentration of the tested inhibitors. Finally, we can conclude that the net decrease of weight loss in the presence of MPE and MPO is an importance sign that these compounds under investigation are efficient inhibitors of mild steel in test solutions.

### 3.6.2. Polarization curves

In order to gain information about the kinetics of the anodic and cathodic reactions, polarization study has been carried out. The representative potentiodynamic polarisation curves of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the presence and the absence of various concentrations of the tested inhibitors are shown in Figs 1. The corrosion parameters including corrosion current densities ( $I_{\text{corr}}$ ), potential ( $E_{\text{corr}}$ ), cathodic Tafel slope ( $\beta_c$ ) and inhibition efficiency ( $E_I$  %) are listed in Table 6.



**Figure 1.** Cathodic and Anodic polarisation curves of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the presence of M. Pulegium oil and extract at different concentrations.



**Table 6.** Electrochemical parameters of steel at various concentrations of MPE and MPO respectively in 0.5 M H<sub>2</sub>SO<sub>4</sub> and the corresponding inhibition efficiencies.

Inhibitors	Concentrations (g/l)	E <sub>corr</sub> (mV)/SCE	b <sub>c</sub> (mV/dec)	I <sub>corr</sub> (mA/cm <sup>2</sup> )	E%
blank	0.5 M	-506	-194	0,9017	-
Mentha pulegium oil	0,5	-504	-149	0,5871	34,8
	1	-486	-164	0,3810	57,7
	2	-487	-147	0,1661	81,6
	4	-480	-146	0,1037	<b>88,5</b>
Mentha pulegium Extract	0.25	-491	-156	0,4071	54,8
	0.5	-474	-159	0,2787	69,1
	1	-472	-161	0,2307	74,4
	2	-482	-143	0,1428	<b>84,1</b>

In this case, the inhibition efficiency is defined as follows:

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

where  $I_{corr}$  and  $I'_{corr}$  are, respectively the uninhibited and inhibited current density. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines. As it can be seen from Figure 1, the addition of M. pulegium inhibitors to the aggressive media inhibit both cathodic and anodic reactions and this inhibition is more pronounced with increasing inhibitors concentrations. These results reveal that the addition of inhibitors reduce the anodic dissolution of carbon steel and also retard the hydrogen evolution reaction. Cathodic current potential curves give rise to parallel Tafel lines indicates that the hydrogen evolution reaction is activation-controlled and the reduction of H<sup>+</sup> ions at the carbon steel surface occur mainly through a charge transfer mechanism. The corrosion potential values were found to fluctuate within a range of [-506, -472] (mV) / SCE. However, we conclude that the corrosion potential values are remaining practically constant by the addition of different concentrations in the presence of inhibitors compared to that in its absence. Based to Ferreira and others [41, 42], if the displacement in E<sub>corr</sub> values (i) >85 mV in inhibited system with respect to uninhibited, the inhibitor could be recognized as cathodic or anodic type and (ii) if displacement in E<sub>corr</sub> is <85 mV, it could be recognized as mixed-type. Since the small displacement of the corrosion potential was about 34 mV (Table 4) towards anodic region, indicating that the studied MPO and MPE are mixed-type inhibitors with predominant anodic effectiveness for MPO. From the electrochemical parameter values given in Table 3 it can be found that:

- $I_{corr}$  were progressively reduced in the presence of inhibitors with steady increase in the concentration from 0.90 to 0.14 and 0.10 mA/cm<sup>2</sup>.
- The best efficiency obtained in the presence of MPE is **88.5%** at 4g/L.
- The best efficiency obtained in the presence of MPO is **84.1%** at 2g/L.

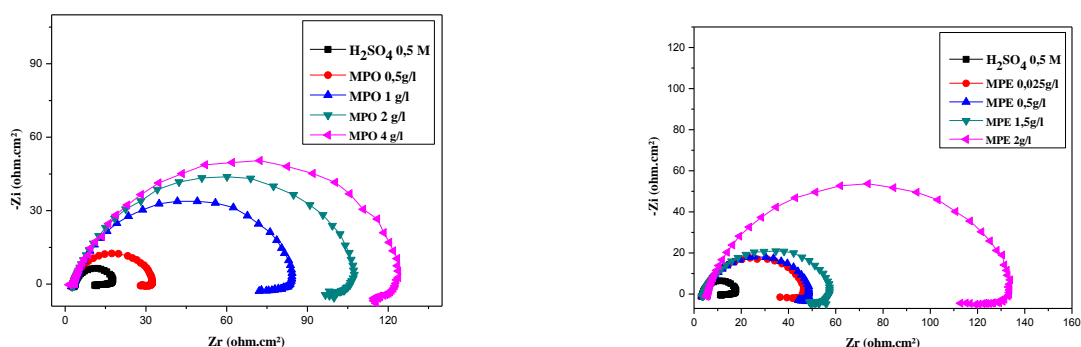
### 3.7. Electrochemical impedance spectroscopy measurements

In order to evaluate E<sub>i</sub>%, the corrosion measures of M. pulegium in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, are also investigated by the EIS at 308 K after 30 min of immersion. The representative Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing different concentrations of MPO and MPE are shown in Figure 2. The EIS data shows that the diameter of each Nyquist Plot semicircle gradually increases. This fact is attributed to the increase in the number

of inhibitive molecules present in the inhibitors when the concentration was increased from 0.25 to 4 g/L. This increase of the diameters has obviously shown that the  $R_t$  values were also increased from 17 to 124 and 129  $\Omega\text{cm}^2$  for MPO and MPE, respectively. The single semicircle indicates that charge transfer takes place at electrode/electrolyte interface, and the corrosion reaction of steel is controlled by the transfer process [43]. Also, these loops are not ideal semicircles; this is associated to the frequency dispersion as a result of the roughness and inhomogeneity of the electrode surface [44]. Based on the EIS data analyzed, the impedance response of mild steel has considerably changed after the addition of MPO and MPE. Table 5 shows the charge-transfer resistance ( $R_t$ ) values which are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [45], the double layer capacitance ( $C_{dl}$ ) and the frequency at which the imaginary component of the impedance is maximal ( $-Z_{\max}$ ) are found as represented in equation:

$$C_{dl} = \frac{1}{2\pi \cdot f_m \cdot R_t} \quad (3)$$

With  $C_{dl}$  : Double layer capacitance ( $\mu\text{F}\cdot\text{cm}^{-2}$ ) ;  $f_m$  : maximum frequency (Hz) and  $R_{ct}$  : Charge transfer resistance ( $\Omega\cdot\text{cm}^2$ ).



**Figure 2.** Nyquist diagrams for steel electrode with and without *M. pulegium* inhibitors.

**Table 7.** Impedance parameters for corrosion of steel in acid at various contents of MPO and MPE respectively.

Inhibitors	Concentrations (g/L)	$R_t$ ( $\Omega\text{cm}^2$ )	$f_{\max}$ (Hz)	$C_{dl}$ ( $\mu\text{F}\cdot\text{cm}^{-2}$ )	E%
Blank	1M	17	-	-	-
Mentha pulegium oil	0.5	30	79.3	66.9	43.3
	1	82,6	31.6	60.9	79.4
	2	106	20.0	75.0	83.9
	4	124	15.8	81.2	<b>86.3</b>
Mentha pulegium extract	0.25	43	40.0	92.5	60.4
	0.5	45	50.0	70.73	62.2
	1	54	40.0	73.6	68.5
	2	129	31.6	39.0	<b>86,8</b>

Parameters such as  $R_t$ , double layer capacitance ( $C_{dl}$ ) and  $E_R\%$  are listed in table 7. It is noticeable that the values of inhibition's efficiency increases with inhibitors concentrations to reach a maximum value 86,3% and 86,8% at 4g/L and 2g/L for MPO and MPE, respectively. The adsorption of inhibitive molecules on the mild steel surface and the



decrease of its roughness can be justified by the gradual variation in values of  $C_{dl}$  from 39 to 92.5  $\mu\text{F}/\text{cm}^2$  at different concentrations. The values of  $E_R\%$  were calculated by the equation as follows:

$$E_R\% = \frac{R'_i - R_i}{R'_i} \times 100 \quad (4)$$

### 3.8. Effect of temperature

The effect of temperature in inhibition reaction is highly complex. In fact, the temperature can modify the interaction between the mild steel and the acid medium such as rupture, desorption of inhibitor and the decomposition and/or rearrangement of inhibitor [46]. To evaluate the influence of temperature on corrosion and corrosion inhibition processes, the weight loss measurements were performed at 313–343 K temperature range. The corresponding results are given in Table 8. Data illustrated in Table 8, shows that in the absence and the presence of different inhibitors the increase of corrosion rate is more pronounced with the rise of temperature and the inhibition efficiency decreases to reach a value of 35.9% and 62% at 343 K for MPO and MPE at 1h immersion period. On the other hand, the slightly decrease on inhibition efficiency with temperature can be justified by the decrease of the strength of adsorption processes at high temperature [47]. From this result, we can deduce that MPO and MPE are excellent inhibitors.

**Table 8.** Inhibition efficiency obtained from the corrosion rate at 2g/L and 4g/L of different inhibitors in 0.5 M  $\text{H}_2\text{SO}_4$  at different temperatures at 1h immersion period.

T(K)	Blank	MPE	MPE	MPO	MPO
	W	W	E%	W	E%
313	0.89	0.25	71.9	0.20	76.8
323	1.35	0.54	60.0	0.47	65.2
333	2.85	1.34	52.9	1.36	52.3
343	5.83	3.28	43.7	3.73	36.0

#### 3.8.1. Kinetic-thermodynamic parameters

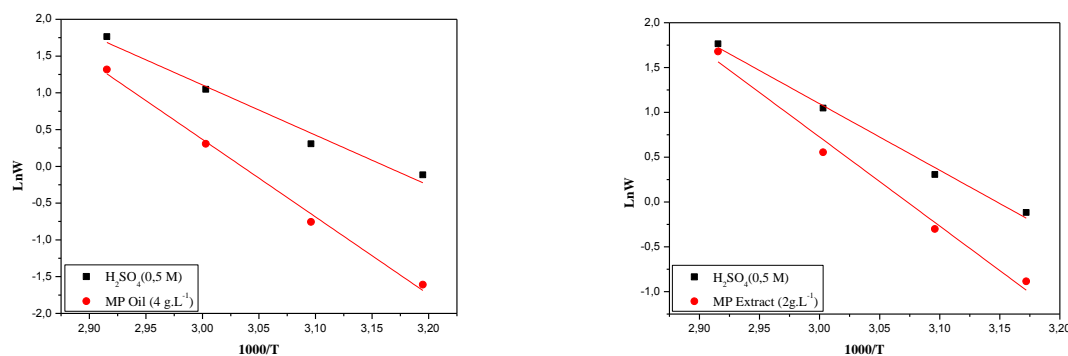
To elucidate the inhibition properties of inhibitors, the kinetic model was practical tool to make clear the mechanism of corrosion inhibition for the inhibitors. The activation parameters for the corrosion process of mild steel in the absence and presence of different concentrations of Pennyroyal were calculated from Arrhenius Eq. (5) and transition state Eq. (6) in the temperature range from 313 to 343 K [48]:

$$\ln W = \ln A - \frac{E_a}{RT} \quad (5)$$

where  $E_a$  represents the apparent activation energy,  $R$  gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor and  $W$  the corrosion rate, obtained from the weight loss method.

$$\ln W = \left[ \ln \left( \frac{RT}{Nh} \right) + \left( \frac{\Delta S_a^\circ}{R} \right) \right] - \frac{\Delta H_a^\circ}{RT} \quad (6)$$

where  $W$  refers to the corrosion rate,  $R$  the gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor,  $h$  is Plank's constant and  $N$  is Avogadro's number. Arrhenius plots for the corrosion rate of mild steel are given in Figure 3. Values of  $E_a$  for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  in the absence and the presence of various concentrations of MPE and MPO were determined from the slopes of  $\ln W$  versus  $1000/T$  plots. All the linear regression coefficients are close to 1, indicating that corrosion of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  can be elucidated using the kinetic model.

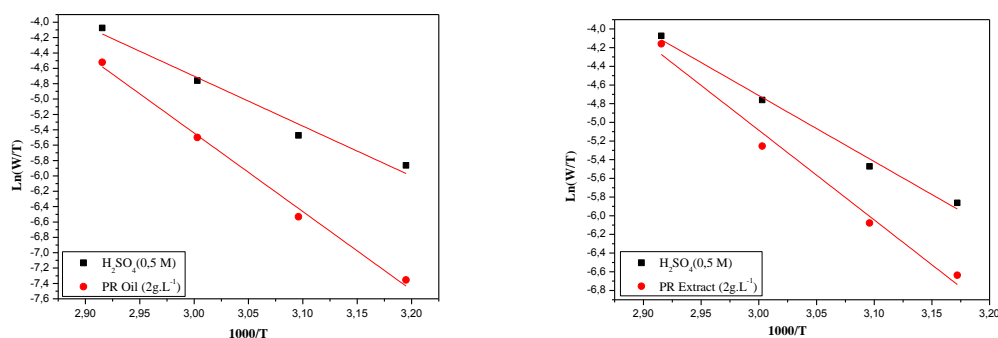


**Figure 3.** Arrhenius plots of mild steel for 2 g/L and 4g/L of MPE and MPO in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Table 9.** Activation parameters for steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of MPE and MPO.

Inhibitors	$\Delta H_a$ k j.mol <sup>-1</sup>	$\Delta S_a$ j.K <sup>-1</sup> .mol <sup>-1</sup>	E <sub>a</sub>
Blank	56.45	-67.83	59.44
MP Extract	94.53	38.35	97.44
MP Oil	84.96	12.05	84.90

It is obvious from data listed in table 9 that, E<sub>a</sub> values increases slightly in the presence of MPO and MPE that indicates the good performance of these inhibitors at higher temperatures and strong adsorption of the inhibitor molecules at the metal surface [49]. The range of E<sub>a</sub> values (84.90-97.44kJ/mol) are higher than the threshold value of 80 kJ/mol, required for chemical adsorption. This means that the adsorption is chemical adsorption. The relationship between Ln(W/T) and 1000/T is shown in Fig. 4. Straight lines are obtained with a slope of  $(-\Delta H_a / R)$  and an intercept of  $((\ln R / N_h + \Delta S_a / R))$  from which the values of  $\Delta H_a$  and  $\Delta S_a$  are calculated and are given in Table 7. Examination of these data reveals that the  $\Delta H_a$  values for dissolution reaction of mild steel are higher in the presence of M. pulegium inhibitors (84,96– 94,53kJ.mol<sup>-1</sup>) than that in its absence (56,45 kJ.mol<sup>-1</sup>).



**Figure 4.** The variation of Ln (W/T) ~ f (1000/T) of the steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> with and without MPE and MPO.

The positive values of  $\Delta H_a$  reflects the endothermic nature of metal dissolution process. It is well noticed that the value of E<sub>a</sub> is larger than the analogous value of  $\Delta H_a$  indicating that the corrosion process involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [50]. Moreover, for MPE the average difference value of the  $E_a - \Delta H_a$  is 2.91 kJ/mol, which is approximately equal to the average value of RT (2.61 kJ/mol). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterized by the following equation:

$$E_a = \Delta H_a - RT \quad (7)$$

Large and negative values of entropy of activation  $\Delta S_a$ , show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. This behavior can be explained as a result of the replacement process of water molecules during adsorption of M. pulegium inhibitors on mild steel surface [51]. It is clear from data listed in Table 9, that  $\Delta S_a$  increased in the presence of the studied inhibitors compared to free acid solution.

### 3.8.2. Adsorption isotherm

Interaction between the organic compounds and metal surfaces can be provided essential information about the adsorption isotherms. The values of surface coverage  $\theta$ , corresponding to different concentrations of inhibitors at 298 K have been used to elucidate the best isotherm to determine the adsorption isotherm. The adsorption isotherms commonly considered were [52]:

Temkin isotherm

$$\exp(f, \theta) = k_{ads} \cdot C \quad (8)$$

Langmuir isotherm

$$\frac{\theta}{1-\theta} = k_{ads} \cdot C \quad (9)$$

Frumkin isotherm

$$\frac{\theta}{1-\theta} \cdot \exp(-2 f \cdot \theta) = k_{ads} \cdot C \quad (10)$$

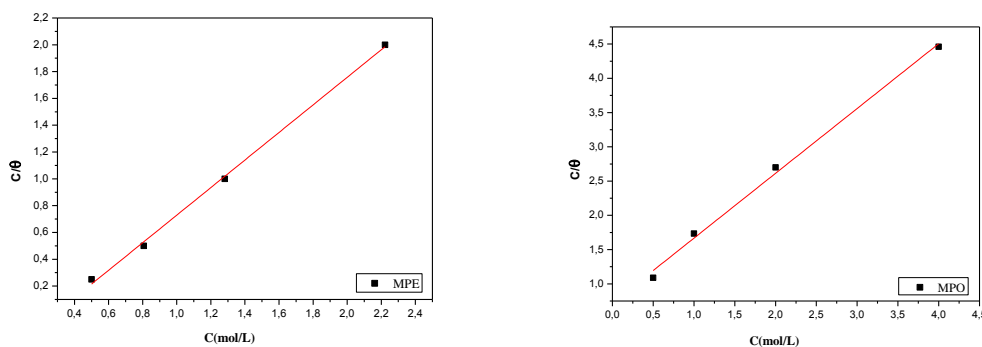
Freundluich isotherm

$$\theta = k_{ads} \cdot C \quad (11)$$

$$\text{With } K = \frac{1}{55.5} \cdot \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (12)$$

Where  $C$  is the inhibitor bulk concentration in g/L,  $\theta$  the fraction of the surface covered determined by  $E\%/100$  from weight loss measurements,  $k$  the equilibrium constant,  $\Delta G_{ads}$  is the standard free energy of adsorption reaction,  $R$  is the universal gas constant,  $T$  is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution in mol/L. Figure. 5 show the dependence of the ratio  $C/\theta$  as function of  $C$  for MPE and MPO respectively.

To gain knowledge about adsorption isotherm obeyed by this system, a graphic relation between the inhibitor concentration  $C_{inh}$  and  $C_{inh}/\theta$ , is drawn and represented in Figure. 5. Straight line with almost unit slope and correlation coefficient ( $0.99775 \leq R \leq 0.99423$ ) were obtained indicating that the system model follows Langmuir adsorption isotherm (Eq. (9)). This indicates also, that mono-layer of the studied inhibitor must have been adsorbed to mild steel surface without interaction between the adsorbed molecules.



**Figure 5.** Plots of Langmuir adsorption isotherm of MPE and MPO on the steel surface at 308 K.

## 4. Conclusion

In this work, we have studied the corrosion behaviour of mild steel in sulfuric acid media taking account the effect of the addition of natural *M. pulegium* (PM) oil and extract at different concentrations and the variation of medium temperature. From the given results, we can have the following conclusions:

- The GC/MS analysis of essential oil isolated from *M. pulegium* (PM) plant shows that its composition is dominated by 1,8-Cineole, piperitone, Limonene and  $\beta$ -Pinene (31.9%, 15.6%, 14.6% and 4.8%, respectively).
- The results of the present study showed that poly-phenolic extract have moderate free radical scavenging activity.
- The inhibition efficiency of MPE and MPO increases with the increase of inhibition concentration and decreases with the rise of temperature.
- MPE and MPO act as mixed-type inhibitors without modifying the mechanism of hydrogen evolution.
- The adsorption of inhibitors on mild steel surface in  $H_2SO_4$  solution follows Langmuir isotherm for both inhibitors MPE and MPO.
- The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results.
- *M. pulegium* (PM) inhibitors being natural and environmentally benign products, they can be used as an alternative for toxic chemical inhibitors in acidization and acid pickling of mild steel.

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