Inhibition of tinplate corrosion in 0.5 M $H_2C_2O_4$ medium by Mentha pulegium essential oil

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Abstract

Considering the great interest of the application of secondary metabolites of medicinal and aromatic plants in several fields, including the control of metal corrosion in different environments and in order to minimize the use of synthetic inhibitors, which is the objective of our research. In this work, we are interested by identifying the chemical profiling of *Mentha pulegium* essential oil and evaluating its effect as a new solution against corrosion in tinned cans. For this purpose, the inhibitory effect of *Mentha pulegium* essential oil against tinplate corrosion in 0.5 M H₂C₂O₄ medium was studied using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurement techniques. The CG and CG-Ms show that the Pulegone and the Menthone are the main compounds of *Mentha pulegium* essential oil. The weight loss measurement and electrochemical tests show that *Mentha pulegium* essential oil exhibits a good anticorrosion effect with an inhibition efficiency of 80% at 4 g/L⁻¹. This effect could be attributed to the adsorption of *Mentha pulegium* essential oil compound on metal surface, which is confirmed by scanning electron microscopy spectroscopy and energy dispersive X-rays (SEM-EDX) visualization.

Keywords: Mentha pulegium, essential oil, canned food, corrosion effect, tinplate, SEM-EDX.

Received: January 23, 2020. Published: January 31, 2020 doi: <u>10.17675/2305-6894-2020-9-1-9</u>

1. Introduction

Since a long time, tinplate represents dominant material used for packaging. This material is a sandwich in which the corps is a sheet of steel coated in both sides with pure tin. In fact, the combination between the strength and formability of steel, the good appearance and the corrosion resistance of tin, makes the tinplate the widely used material as food and beverage packaging material. However, the shelf life of cans and nutritional values of the canned food can be influenced by many factors [1]. Some of them are principally due to

corrosion phenomena resulting from the interaction between the metallic material and the can contents, also the tin coating masses, the type of food product, the presence of corrosion accelerators or inhibitors in the product, in addition to the temperature and storage time [2]. The corrosion influences not only the commercialization of the canned product but also its quality. This phenomenon can be a source of food contamination by tin and iron. The tin maximum limit in canned food is 250 mg \cdot kg⁻¹ for solid and 150 mg \cdot kg⁻¹ for beverages, for iron the level accepted is 20 to 50 mg \cdot kg⁻¹ [3].

Most fruits and vegetables intended for canned storage contain natural oxalic acid [4, 5]. Indeed, this organic acid is added to canned fruits to increase the tartness and enhance their flavor [6]. The oxalic acid is also an antioxidant agent [6] but its high acidity may cause cans corrosion [7, 8].

To reduce the negative effect caused by the acidity of food in cans, many methods were tested, such as the chemical treatment of tinplate [9], passivation treatment [10], coating protection and the use of synthetic inhibitors. The later showed good inhibition efficiency [11]. However, those compounds induce many negative effects on environment and health; therefore it is necessary to find a new alternative that can be accessible, simple and ecologic.

For this, the use of natural compounds represents a safe and an alternative method used against the corrosion of food cans. Many studies confirm that oils or extract of natural plants show good inhibition efficiency against tinplate corrosion. Those compounds are eco-friendly and less expensive than synthetic inhibitors. In this context, the essential oil of *Ammodaucus leucotrichus* is able to reduce the corrosion of tinplate on 0.5 M H₂C₂O₄ [12]. Bammou *et al.* found that *Thymus satureioides* essential oils inhibit the corrosion of tinplate in 0.5 M HCl [13]. Also, the *Artemisia* essential oils show a good effect against the corrosion of tinplate in acid medium [14]. The onion essential oil may be active against the corrosion of tinplate in contact with tomato puree [15].

In the same way, this work represents a continuity of studies starting in our laboratory, which are focused on the valorization of medicinal and aromatic plants growing in Draa-Tafilalet region (Morocco) by studying the possibility of their introduction in agroalimentary sectors. Consequently, we are interested to evaluate the inhibition effect of *Mentha pulegium* essential oil, which is known by its medicinal proprieties [16, 17] and its high contents of essential oil [18], also its anticorrosion activity [19, 20, 21], using gravimetric and electrochemical impedance spectroscopy and electrochemical polarization measurements. The surface morphology was visualized using scanning electron microscopy spectroscopy and energy dispersive X-rays (SEM-EDX).

2. Material and methods

2.1 Plant material and Essential oil isolation

The aerial part of *Mentha pulegium* (*Lamiaceae* family) was harvested in Errich near Errachidia, Morocco on June. The aerial parts of the plant were dried in the dark at room

temperature then grinded. 100 g of obtained powder was hydrodistillated for 3 h using Clevinger-type apparatus according to the European Pharmacopoeia method. The yield of the essential oil obtained is 2% based on dried weight sample. The obtained essential oil was stored in the dark at 4°C.

2.2 Essential oil analysis

2.2.1 GC analysis

GC analysis were conducted using a Perkin-Elmer Autosystem XL GC apparatus equipped with dual flame ionization detection (FID) system and fused-silica capillary columns (60 m x 0.22 mm I.D., film thickness 0.25 μ m), Rtx-1 (polydimethylsiloxane). The oven temperature was programmed from 60°C to 230°C at 2°C/min and then held isothermally at 230°C for 35 min. The temperature of the injector and detector was maintained at 280°C. A volume of 0.2 μ L of pure oil was injected in the split mode (1/50) and the helium was used as carrier gas (1 mL/min).

2.2.2 GC-MS analysis

A volume of $0.2~\mu L$ of MPEO was analyzed using a Perkin-Elmer Turbo mass detector (quadrupole), coupled to a Perkin-Elmer 88 Autosystem XL, using Helium as carrier gas (1 mL/min). The ion source temperature was 150°C, the temperature of the oven was programmed from 60°C to 230°C at 2°C/min and then held isothermally at 230°C (35 min). The injector temperature was fixed at 280°C, the energy ionization at 70 eV, electron ionization mass spectra were acquired over the mass range 35–350 uma, split: 1/80.

2.3 Gravimetric test

The weight loss measurement are carried out under total immersion of tinplate of (1.5 x 1.5 cm²) with the chemical composition Sn (51.49%), Fe (47.23%), Co (0.88%) and Al (0.41%), in 50 ml of 0.5 M H₂C₂O₄ solution with different concentration of MPEO. Before the immersion of tinplate sheets into the aggressive medium, the sheets were rinsed with distillated water, digressed with ethanol then derided and weighted. After 6 hrs of immersion at 303°K, the samples were rinsed, dried and weighted. To evaluate the effect of temperature and the thermodynamic parameters, the same tests were conducted in range temperature 303 to 374°K for 2 hrs of total immersion in corrosive medium with different concentrations of essential oil.

The rate corrosion $W(\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1})$ is calculated according to the Equation (1):

$$W = \frac{m_0 - m_{\text{inh}}}{St} \tag{1}$$

With, m_0 and m_{inh} represent the sheets weight before and after immersion, $S(\text{cm}^2)$ represents simple surface and t(h) duration of immersion.

The inhibition efficiency E% is determined according to the Equation (2):

$$E\% = \frac{W_0 - W_{\text{inh}}}{W_0} \cdot 100 \tag{2}$$

 W_0 and W_{inh} represent the corrosion rate in the absence and presence of inhibitor, respectively.

The coverage surface θ is calculated using Equation (3):

$$\theta = (1 - \frac{W_{\text{inh}}}{W_0}) \tag{3}$$

2.4 Electrochemical impedance spectroscopy

The electrochemical study was conducted using potentiostat Volta lab PGZ 100. This potentiostat is piloted by Volta master software connected to a cell with three electrodes; the saturated calomel electrode and platinum electrode were used as reference and auxiliary electrode and the same material used in gravimetric test was used as working electrode. The sheets of tinplate are cut to obtain a disc with surface area of 0.5 cm².

The working electrode was rinsed with distilled water, digressed with acetone and dried before its immersion in oxalic acid solution with different concentration of *Mentha pulegium* essential oil. Before all measurement, the working electrode was established at open circuit potential ($E_{\rm ocp}$) for 30 min. After measuring $E_{\rm ocp}$, all electrochemical tests were conducted at ambient temperature.

The electrochemical impedance spectroscopy were carried out at rest potential $E_{\rm ocp}$, with sine wave voltage (10 mV) peak to peak, and frequency range with 100 KHz as high limit and 10 mHz as low limit. The value of $R_{\rm t}$ and $C_{\rm dl}$ were obtained from the Nyquist plot.

The inhibition efficiency (E_R) is calculated according to the following Equation (4):

$$E_{\rm R} = \left(\frac{R_{\rm inh} - R_0}{R_{\rm inh}}\right) \cdot 100 \tag{4}$$

 R_{inh} represents the charge transfer in presence of MPEO and R_0 is the charge transfer without addition of MPEO.

2.5 Potentiodynamic polarization test

The potentiodynamic polarization tests were conducted at ambient temperature with and without addition of MPEO in $0.5 \text{ M C}_2\text{H}_2\text{O}_4$ solution. Potentials were recorded at scan rate of 1 mV/sec in cathodic and anodic direction from the corrosion potential (E_{corr}). The Tafel extrapolation method allows us the determination of corrosion current densities in the presence of different MPEO concentrations.

The inhibition efficiency in function of corrosion current density (E_I %) is calculated according to the followed Equation (5):

$$E_{\rm I}\% = \left(\frac{I_0 - I_{\rm inh}}{I_0}\right) \cdot 100\tag{5}$$

 I_0 and I_{inh} represent the corrosion current densities in the presence and absence of MPEO respectively.

2.6 Scanning electron microscopy and energy dispersive X-rays (SEM-EDX)

The morphology of the corrosion products formed on tinplate surface in $0.5 \text{ M H}_2\text{C}_2\text{O}_4$ solution with and without addition of the optimal concentration of MPEO, were examined by SEM-EDX using a TESCAN VEGA 3 EDAX instrument at an accelerating voltage of 20 kV. After 6 h of tinplate samples immersion in $0.5 \text{ M H}_2\text{C}_2\text{O}_4$ solution in the presence and absence of $4 \text{ g} \cdot \text{L}^{-1}$ MPEO, the tinplate samples were washed with distilled water then dried before their visualization using SEM-EDX.

3. Result and discussion

3.1 CG and CG-MS analysis

The qualitative and quantitative analyses of *Mentha pulegium* essential oils were conducted using GC and GC/MS analyses. The chemical composition of the studied essential oil is shown in the Table 1.

Table 1. The chemical composition of *Mentha pulegium* essential oil.

N	Components	<i>RI</i> apol	<i>RI</i> pol	RI lit	<i>E0</i> %
1	α-Pinene	930	1023	936	0.1
2	Myrcene	981	1167	987	0.1
3	Limonene	1021	1208	1024	0.2
4	Menthone	1134	1468	1136	4.8
5	Isomenthone	1143	1494	1146	0.6
6	trans-iso- Pulegone	1150	1587	1161	2.1
7	Neomenthol	1153	1602	1156	3.9
8	α-Terpineol	1175	1694	1176	0.2
9	Pulegone	1215	1654	1215	74.6
10	Neomenthyl acetate	1261	1675	1263	0.6
11	Piperitenone	1316	1918	1318	1,0
12	trans- Caryophyllene	1418	1587	1421	0.3

N	Components	RI apol	<i>RI</i> pol	RI lit	<i>EO</i> %
13	a-Humulene	1451	1675	1455	0.5
14	Mint lactone I	1452	2296		0.5
15	Caryophyllene oxide	1570	1981	1578	0.5
16	Humulene epoxyde II	1594	2038	1602	0.7
Total identification (%)				90.7%	
Oxygenated monoterpenes				87.8%	
Oxygenated sesquiterpenes				1.2%	
Н	lydrocarbon monoterpe	enes		0.4%	
Н	ydrocarbon sesquiterpe	enes		1.3%	

RI lit = retention indices on the apolar column (Rtx-1) in literature;

RI apol = retention indices on the apolar column (Rtx-1);

RI pol = retention indices on the polar column (Rtx-Wax).

The GC and CG-MS analysis allow us the identification of 16 chemical compounds, representing 90.7% of total oil with dominance of oxygenated monoterpenes (87.8%). The Pulegone represents the main compound with 74.6% followed by the Menthone with 4.8% of the oil, Neomenthol with 3.9%, trans-iso-Pulegone with 2.1% and Piperitenone with 1%. The other compounds represent less than 1% for each one. Our study is in accordance with the study conducted by Amalich *et al.* (2016) [22], that confirms that the *Mentha pulgium* essential oil represents a source of Pulegone (71.97%). However, another study shows that the *Mentha pulegium* essential oil is dominated by 1,8-Cineole (31.9%) and piperitenone (15.6%) while the pulegone represents only 2.2% [23]. The chemical variability of *Mentha pulegium* essential oil can be attributed to many factors such as plant genotypes, environmental factors and the plant draying method [24].

3.2 Gravimetric measurements

The inhibition effect of MPEO against the tinplate corrosion in $0.5 \text{ M C}_2\text{H}_2\text{O}_4$ solution was studied using the gravimetric measurement. This method is based on the difference between the weight of samples before and after their immersion into the test solution. The inhibition efficiencies E% in different concentration of MPEO were calculated in the classical way by using the experimental weight loss data. The obtained results are represented in Table 2.

$C \ (\mathbf{g} \cdot \mathbf{L}^{-1})$	$W \ (\mathbf{mg} \cdot \mathbf{cm}^{-2} \cdot \mathbf{h}^{-1})$	E %	Θ
0	0.56		
0.5	0.30	45.14	0.45
1	0.26	53.50	0.54
2	0.16	72.04	0.72
3	0.14	74.46	0.74
4	0.11	80.32	0.80

Table 2. Gravimetric result of tinplate in 0.5 M C₂H₂O₄ solution with various concentration of MPEO.

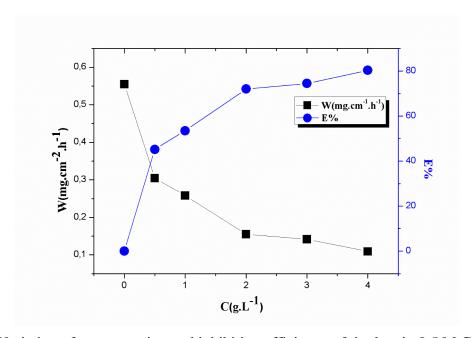


Figure 1. Variation of rate corrosion and inhibition efficiency of tinplate in $0.5 \text{ M C}_2\text{H}_2\text{O}_4$ solution in the presence of MPEO with various concentrations.

As shown in Table 2 and Figure 1, the addition of MPEO into 0.5 M $\rm H_2C_2O_4$ reduces the rate corrosion, inducing the increase of the inhibition efficiency. The inhibition effect of MPEO depends on the concentration used. For this purpose, we notice that the optimum inhibition efficiency is observed at 4 g·L⁻¹ with E% = 80.32%. This inhibition efficiency can be attributed to the increase of covered surface Θ , resulting from the adsorption of MPEO compounds on tinplate surface and blocking the active sites, thus protecting the tinplate surface attacked by active corrosion ions.

3.3 Adsorption isotherm

MPEO compounds prevent the corrosion process by their adsorption on the metal surface with displacement reaction inducing removal of a number of the adsorbed water molecules

from the metal surface. This adsorption never reaches the real equilibrium and tends to an adsorption steady state [25]. In this way, a several conditions are responsible on the adsorption of the inhibitor on metal surface, such as the inhibitor electronic characteristics, the metal surface nature, temperature and the varying degrees of surface-site activity [26].

The dependence of the surface covered Θ as function of MPEO concentration used $C(g \cdot L^{-1})$ is graphically fitted in Figure 2.

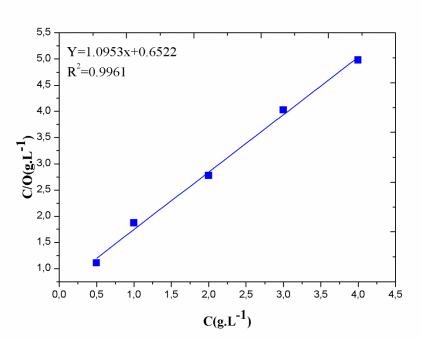


Figure 2. Langmuir adsorption isotherm plot of MPEO on tinplate in 0.5 M C₂H₂O₄ solution.

The obtained curve shows clearly that it fits well with Langmuir isotherm adsorption according to the mathematical relationship (7):

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \tag{7}$$

 $K_{\rm ads}$ represents the adsorption equilibrium constant.

In the literature, Langmuir isotherm assumes that the equivalence of adsorption sites in each site is able to adsorb only one molecule [27].

3.4 Effect of temperature and activation thermodynamic parameters

The investigation of the effect of temperature on tinplate corrosion in $0.5 \, M \, H_2 C_2 O_4$ solution in the presence of MPEO, was conducted using gravimetric test at range temperature (303–373). The obtained results are presented in Table 3.

	31	3°K	32	3°K	34	3°K	37	3°K
$C(\mathbf{g}\cdot\mathbf{L}^{-1})$	<i>W</i> *	E (%)						
0.5 M H ₂ C ₂ O ₄	0.79		1		1.5		2	
0.5	0.59	26.32	0.76	24.05	1.15	23.32	1.54	22.72
1	0.43	45.60	0.59	40.78	0.91	39.34	1.30	34.89
2	0.30	62.14	0.40	59.49	0.72	52.18	0.99	50.45
3	0.26	67.16	0.36	63.64	0.60	59.60	0.82	58.89
4	0.16	79.72	0.29	70.83	0.49	67.19	0.66	66.23

Table 3. Temperature effect on tinplate corrosion in 0.5 M C₂H₂O₄ solution with addition of MPEO with various concentrations.

From the data shown in Table 3, it is clear that the corrosion rate depends on the temperature, meaning that the increase of temperature induces the rise of rate corrosion. Also, the inhibition efficiency decrease with the increase of the temperature, the inhibition efficiency is of 80.32% at temperature 303°K at the optimum concentration, however at the same concentration the inhibition efficiency is 66.23% at 373°K.

The activation thermodynamic parameters of the corrosion process are calculated using the Arrhenius Equations (7) and (8):

$$W = K \exp\left(\frac{E_{\rm a}}{RT}\right) \tag{7}$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{a}}{R}\right) \exp\left(\frac{-\Delta H_{a}}{RT}\right)$$
 (8)

W represents the tinplate rate corrosion, E_a is the apparent activation energy, ΔS_a is the entropy of activation, ΔH_a represents the enthalpy of activation, K is the Arrhenius pre-exponential factor, h is the Plank's constant and N is the Avogrado's number.

The activation energy values are determined from the corresponding slope of straight lines of Arrhenius plots Figure 3(a), where the slope represents $(-E_a/R)$. Concerning the enthalpy ΔH_a and the entropy of activation ΔS_a are determined from the slope $(\Delta H_a/R)$ and the intercept $(\ln R/Nh + \Delta S_a/R)$ of straight lines in Figure 3(b).

From the Table 4, it is clear that the activation energy in the presence of MPEO $(4 \text{ g} \cdot \text{L}^{-1})$ is higher than the one obtained for oxalic acid only. This is attributed to the physisorption mechanism of MPEO on tinplate surface [28, 29], reflecting the formation of an adsorption film of physical nature (electrostatic) [30].

^{*} $W (\text{mg} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}).$

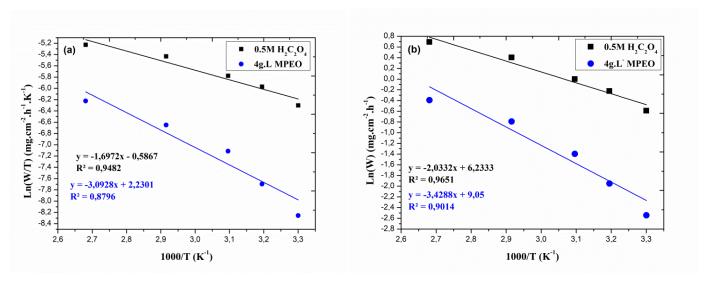


Figure 3. Tinplate Arrhenius plots in 0.5 M $H_2C_2O_4$ solution with and without addition of the optimum concentration 4 g·L⁻¹ of MPEO.

Table 4. Activation parameters of tinplate corrosion in $0.5 \text{ M H}_2\text{C}_2\text{O}_4$ solution in the presence and absence of the optimum concentration of MPEO.

$C \ (\mathbf{g} \cdot \mathbf{L}^{-1})$	E_{a} $(\mathrm{kJ \cdot mol}^{-1})$	ΔH_{a} $(\mathbf{kJ \cdot mol}^{-1})$	$\Delta S_{\mathbf{a}}$ $(\mathbf{k}\mathbf{J}\cdot\mathbf{mol}^{-1})$
0.5 M H ₂ C ₂ O ₄	16.90	14.11	-83.29
4	24.78	22.01	-70.37

As shown in Table 4 the enthalpies values (ΔH_a) are positive in the presence and absence of optimum concentration of MPEO (4 g·L⁻¹), this means that the dissolution of tinplate process obeys to endothermic nature reflecting that its dissolution is difficult [31]. The high value observed in the presence of essential oil indicate its high protection compared to the uninhibited solution, this increase in enthalpy is attributed to the process of inhibitor adsorption [32]. The value of E_a – ΔH is 2.79 around the average value of RT at 331°K, the average temperature of the studied domain which affirms that the corrosion process is unimolecular reaction by the known of a perfect gas [33]. However, the negative values of entropies (ΔS_a) in the presence and absence of MPEO suggest that the activated complex are in association than a dissociation, meaning that a decrease in disordering takes place on going from the reactant to the activated complex [34].

3.5 Electrochemical impedance spectroscopy

We used the electrochemical impedance spectroscopy (EIS), to get information about the characteristics and kinetics of the electrochemical processes taking place at material/acid interface, also, to evaluate the effect of MPEO against the corrosion mechanisms. This method repose on applying frequencies and low amplitude sinusoidal voltage wave in

order to produce perturbation signals on the working electrode. The Figure 4 shows the Nyquist diagrams of tinplate obtained at E_{ocp} in 0.5 M $H_2C_2O_4$ solution with and without addition of different concentration of MPEO.

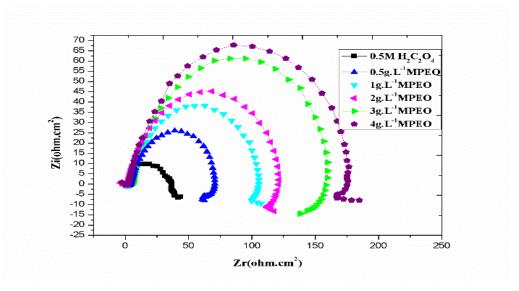


Figure 4. Nyquist diagrams for tinplate in 0.5 M H₂C₂O₄ in presence of MPEO with various concentration.

Table 5. Impedance parameters for corrosion of tinplate in oxalic acid with and without addition of MPEO.

$C \ (\mathbf{g} \cdot \mathbf{L}^{-1})$	$R_{ m t} \ (\Omega \cdot { m cm}^2)$	$C_{ m dl} \ (\mu ext{F} \cdot ext{cm}^2)$	E _R %
0.5 M H ₂ C ₂ O ₄	39.54	85.32	_
0.5	61.34	78.42	35.54
1	105.60	68.31	62.56
2	119.40	67.21	66.88
3	149.30	65.07	73.52
4	181.60	22.84	78.23

As shown in Figure 4, the presence of single loop in Nyquist diagrams means that the corrosion of tinplate in 0.5 M oxalic acid is controlled by charge transfer [35]. It is also necessary to note that the loops have similar form in different conditions, this means that the addition of MPEO have no effect against the corrosion mechanism and inhibits the corrosion primarily through its adsorption on the tinplate surface, which is in accordance with the result obtained by Bouyanzer *et al.* (2006) [19]. In the other hand, the diameters of capacitive loops increase by increasing the concentration of MPEO used; this can be

attributed to the increase of the impedance in inhibited substrate and the formation of protective film on tinplate surface. Which provoking good inhibitive performance.

From the data presented in the Table 5, it is clear that inhibition efficiency increase by increasing the MPEO concentration to reach its high value 78.23% at $4 \, \mathrm{g \cdot L^{-1}}$ and the double layer capacitance (C_{dl}) decreases, this result is attributed to the adsorption of MPEO compounds on tinplate surface.

3.6 Potentiodynamic polarization curves

The polarization measurement was conducted to evaluate the kinetics of cathodic and anodic reactions. The draw of Tafel plot allows as the determination of inhibitor mechanism (Figure 5). The electrochemical parameters also the inhibition efficiency are gartered in Table 6.

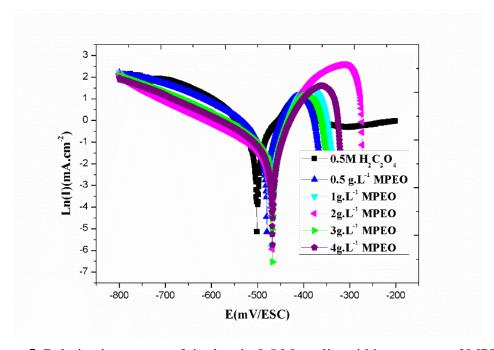


Figure 5. Polarization curves of tinplate in 0.5 M oxalic acid in presence of MPEO.

The result represented in Table 6, show that addition of MPEO decrease corrosion current density, as consequence the inhibition efficiency (E_I %) increase to reach it high value at 4 g·L⁻¹ MPEO. The Figure 5 shows that the addition of MPEO induce a shift in the corrosion potential value to anodic region. This indicate that MPEO blocked the anodic reaction.

Figure 5 shows that the anodic and cathodic branch of polarization curve have the same pace with different concentration of essential oil as well in free acid. In anodic branch, we observe the presence of peak, the last is attributed to the formation of an oxide layer Sn(II) and its oxidation to Sn(IV) [36].

$C \\ (\mathbf{g} \cdot \mathbf{L}^{-1})$	E _{corr} (mV/SCE)	I _{corr} (mA/cm²)	$\begin{array}{c} \beta_a \\ (mV) \end{array}$	β _c (mV)	E ₁ %
0.5 M H ₂ C ₂ O ₄	-510.20	1.12	55.10	-227.90	_
0.5	-481.40	0.87	55.10	-213.30	21.93
1	-472.00	0.64	51.90	-218.40	42.60
2	-469.30	0.35	51.40	-213.10	68.37
3	-469.30	0.34	63.50	-236.60	69.78
4	-469.40	0.22	51.30	-229.80	80.35

Table 6. Corrosion parameters of tinplate in oxalic acid with various concentrations of MPEO by using Potentiodynamic polarization method.

From the investigation of the data represented in Table 6, it is clear that the corrosion current density (I_{corr}) decrease by increasing the concentration of essential oil in test solution as consequence the inhibition efficiency (E_I %) increase to reach its high value 80.35% at 4 g·L⁻¹. The addition of this oil move slightly the corrosion potential (E_{corr}) to anodic values. However, the inhibitor is classified based on the displacement of the corrosion potential, if it is higher than 85 mV compared to the one of the free acid, the inhibitor is considered as anodic or cathodic type [37], for us the corrosion potential displacement is only 40.6 mV, so MPEO acts as mixed type inhibitor. In the other hand, the irregular trends of β_a and β_c is due to the adsorption of more than one type of species on tinplate surface, this is attributed to the chemical composition of the essential oil studied [38].

3.7 Scanning electron microscopy (SEM)

MEB-EDX observations of tinplate samples after 6 hours of immersion in $H_2C_2O_4$ 0.5 M at 303°K without and with the addition of the optimal concentration of MPEO are shown in Figure 6 and Figure 7.

From the examination of the SEM plates Figure 6, we observe that the surface of the tinplate after 6 hours of immersion in the acid medium is more attacked. On the other hand, in the presence of MPEO we observe that the tinplate surface is covered with organic products, which is confirmed by the high levels of oxygen in the EDX spectra (Figure 7). From this observation, it can be seen that the inhibition of tinplate corrosion is due to the formation of an adherent deposit, thus protecting the tinplate surface from the aggression of the corrosive environment.

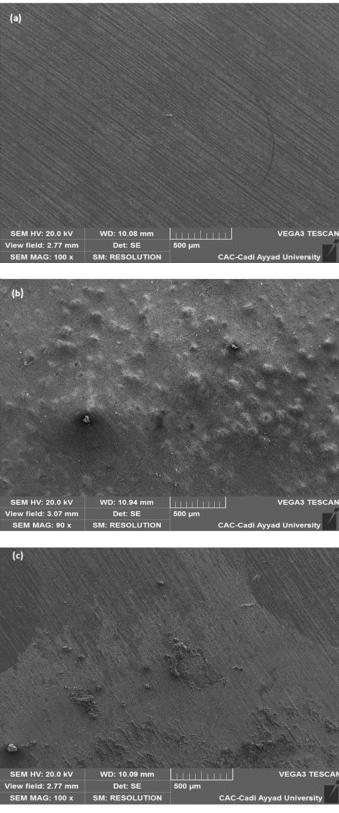


Figure 6. SEM micrographs of tinplate samples at $308^{\circ}K$ (a) tinplate surface before immersion, (b) after 6 h of immersion in 0.5 M $H_2C_2O_4$, (c) after 6 h immersion in 0.5 M $H_2C_2O_4$ with 4 $g\cdot L^{-1}$ MPEO.

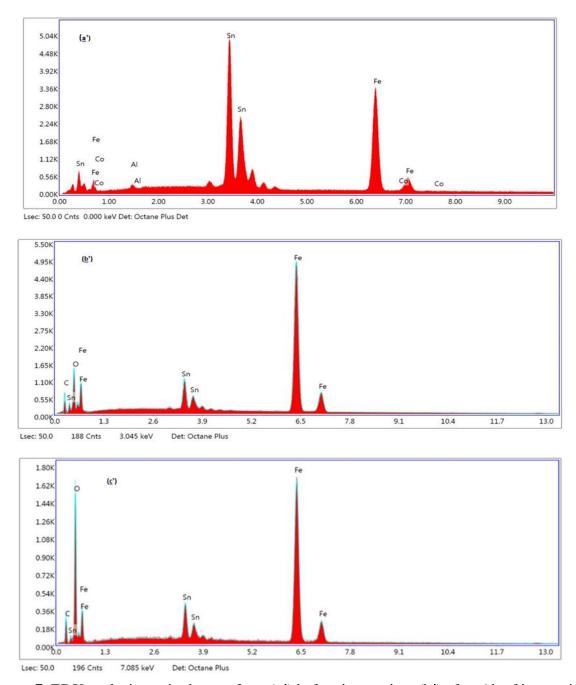


Figure 7. EDX analysis on tinplate surface, (a') before immersion, (b') after 6 h of immersion in 0.5 M $H_2C_2O_4$, (c') after 6 h of immersion in 0.5 M $H_2C_2O_4$ with 4 $g \cdot L^{-1}$ MPEO.

4. Conclusion

From the present study, we conclude that *Mentha pulegium* essential oil acts as a good corrosion inhibitor for tinplate in 0.5 M oxalic acid. This oil shows its high inhibition efficiency at 4 g·L⁻¹ that is due to the adsorption of essential oil main compounds such as polugone (74.6%) and the menthone (4.8%) or synergy between all compounds on tinplate surface. The adsorption of *Mentha pulegium* essential oil was found to obey Langmuir isotherm adsorption. The EIS measurement indicated that the corrosion mechanism of

tinplate is controlled by charge transfer process. The addition of essential oil inhibits the corrosion but doesn't affect the corrosion mechanism. From the potentiodynamic measurements results we can conclude that the addition of *Mentha pulegium* essential oil reduces the corrosion current density and this oil acts as mixed type inhibitor with an anodic tendency. The MEB-EDX observations are in accordance with the gravimitic and electrochemical analysis. From these results and the medicinal effect of *Mentha puleguim*, we can conclude that this plant can be used in food industry to reduce the effect of cans corrosion and protecting the canned food from contamination by corrosion product such as dissolved tine and iron.

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