

Inhibitive effect of *Thymus satureioides* essential oil as a green corrosion inhibitor for mild steel in an acidic medium

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Abstract

The efficiency of *Thymus satureioides* essential oil (EO) as inhibitor of mild steel corrosion in hydrochloric acid 1.0 M has been studied using polarization curves, electrochemical impedance spectroscopy (EIS) and weight loss measurements. The chemical composition of essential oil was characterized by 29 components, which accounted for 99.24% of the total oil. The major constituents were carvacrol (29.65%), followed by borneol (19.04%), linalool (11.79%), *p*-cymene (8.53%), camphene (7.01%), γ -terpinene (6.10%), α -pinene (4.55%) and caryophyllene (2.39%). The maximum inhibition efficiency (*IE*) (90%) was observed at the optimum concentration of 1.5 g/L. The electrochemical impedance spectroscopy data have shown that the formation of a protective film decrease the double layer capacitance and increases in the charge transfer resistance of mild steel. Increasing temperature reduces surface covered by the inhibitor, which results in a decrease of percentage inhibition efficiency from 89% to 76%. Polarization curves indicated that this EO can be classified as a mixed inhibitor in acidic medium with a predominant anodic inhibition. The value of enthalpy change is positive, which indicated endothermic adsorption process. The inhibition efficiencies calculated by weight loss exhibit a trend parallel to that of polarization and electrochemical impedance spectra measurements. We can conclude that essential oil extracted from *T. Satureioides* may be suggested as a green inhibitor against corrosion under acidic environment.

Keywords: *Thymus satureioides*, essential oil, mild steel, corrosion inhibition.

Received: December 11, 2018. Published: April 11, 2019

doi: [10.17675/2305-6894-2019-8-2-11](https://doi.org/10.17675/2305-6894-2019-8-2-11)

1. Introduction

The use of mild steel is foremost in several industries such as oil and gas and energy generating, possibly due to its superb mechanical properties and comparatively cheaper cost [1, 2]. However, this steel is highly corrodible when exposed to acid solutions, causing severely financial and industrial losses. These acids have an important role in the industry. For instance, essential processes like pickling, descaling and oil well acidizing employ acids such as hydrochloric (HCl) and sulfuric (H₂SO₄) acid solutions [3–5]. There are several methods to protect or prevent metal surface from corrosion, such as barrier protection [6], galvanization [7], cathodic protection [8], *etc.* However, these techniques are often unsuitable when the metal is exposed to a corrosive medium for a long time. Therefore, the use of corrosion inhibitors is one of the most common methods applied for protecting metal or alloy surfaces in acidic environment [9–14].

In the last decades, environment protection became a major concern. In the field of science, researches turned to anything biodegradable and respectful of the environment. In corrosion inhibition field, research has been devoted on corrosion prevention by green inhibitors namely also ecofriendly inhibitors that show good inhibitory effect with low risk of environmental and low cost [1, 2, 10, 15–17]. The *Thymus* species are widely distributed in various regions in Morocco [18]. The percentage of endemism is 46.6%, representing seven species [19]. Among these species, *Thymus satureioides* is an endemic plant of Morocco [20], known under the following vernacular names, in Tamazight “Azukni”, “Tazuknit”, in Arabic “Zaitra” [20].

The purpose of this study is the evaluation of the effectiveness of the flowering tops essential oil of *Thymus satureioides* on steel corrosion in 1.0 M hydrochloric acid, using potentiodynamic polarization curves (PDP), electrochemical impedance spectroscopy (EIS) and gravimetric measurements.

2. Experimental procedure

2.1. Plant materiel and volatile oil isolation

Flowering tops of *Thymus satureioides* were harvested in Taltemssen region (south region of Agadir, Morocco) during the month of May, and then they are air-dried in the shade at ambient temperature for a week. The volatile oil was isolated by hydrodistillation with Clevenger device, according to European pharmacopoeia procedure [21]. The oil obtained was dried with anhydrous sodium sulfate (Na₂SO₄) and then stored in brown bottles at 4 degrees centigrade to avoid its evaporation and decomposition.

2.2. Components identification

The device used is of type: Perkin Elmer Auto System XL, equipped with a flame ionization detector (FID). 0.2 µl of EO are injected using a micro-syringe. Nitrogen (N₂) was used as a vector gas at a flow rate of 1 mL/min. The column used is a capillary

column of Elite type (60 m×0.320 mm), the film thicknesses is 1.0 μm, flow rate of hydrogen (H₂) 35 mL/min, synthetic air flow 350 mL/min, injection temperature 235°C, detection temperature: 240°C. The programming of the temperature of the column is as follows: the initial injection temperature is 50°C for 5 min then rises in increments of 4°C/min at 230°C for 5 min.

2.3. Corrosion study

2.3.1. Steel samples

Mild steel (2.5×2.0×0.2 cm) was used as substrate whose chemical composition is 0.370% C, 0.011% Ti, 0.077% Cr, 0.680% Mn, 0.016% S, 0.059% of Ni, 0.009% of Co, 0.230% Si, 0.160% of Cu and the remainder iron (Fe). The steel surface was mechanically polished using abrasive paper up to 1600 grade. The impurity on the surface was washed with bidistilled water and acetone.

2.3.2. Solution preparation

The aggressive solution is hydrochloric acid solution (1.0 M HCl) prepared from concentrated commercial acid at 37% and double distilled water. The concentrations of EO used in this study were varied from 0.05 to 1.5 g/L.

2.3.3. Gravimetric measurements

In the gravimetric experiment, the metal coupons were immersed 6 hours in 1.0M of hydrochloric solution containing different concentrations of the inhibitor. The metal specimens were immersed in the acidic solution with the help of glass hooks. The specimen weights were noted before immersion. After 6 hours of immersion to HCl medium, the steel specimens were removed, rinsed with bidistilled water, cleaning in acetone, dried at ambient temperature and then weighted. All the values are the means of three measurements. The solution volume is 100 mL.

2.3.4. Electrochemical study

Impedance measurements analyzing are carried out with a mounting comprising a Tacussel potentiostat, type Radiometer PGZ 100, controlled by Voltamaster4 software. Three-electrode consisting of saturated calomel (SCE) as reference electrode, platinum as an auxiliary electrode, and mild steel as working electrode were used for electrochemical test. The specimen (working electrode) was immersed in the experimental solution for 30 minutes until an open circuit potential (E_{ocp}) was obtained. Electrochemical study was performed in air-saturated 1.0 M HCl solution at 303 K.

Intensity–potential curves or polarization curves of the metal–electrolyte interface were recorded from –800 to –200 mV/SCE at constant temperature (303 K) with a sweep of 1 mV·s^{–1}. A thermostated bath was used to maintain the solution temperature at desired temperature. Electrochemical impedance spectroscopic measurements were conducted at

OCP in the frequency range of 10^{-1} Hz to 10^5 Hz and peak-to-peak amplitude of 5 mV was measured with a data density of 10 points per decade.

3. Results and discussion

3.1. Identification of compounds

The oil was analyzed by gas chromatography. In total, 29 components were identified, representing 99.33% of the total oil (Table 1). The oxygenated and hydrocarbon monoterpenes contributed 65.39% and 30.47% in oil sample, followed by sesquiterpenes hydrocarbons and oxygenated sesquiterpenes (3.13% and 0.34%).

The major components of the essential oil were carvacrol (29.65%), followed by borneol (19.04%), linalool (11.79%), *p*-cymene (8.53%), camphene (7.01%), γ -terpinene (6.10%), α -pinene (4.55%) and caryophyllene (2.39%). This composition is close to that given by A. Kasrati *et al.* [22] of the essential oil extracted from aerial parts of *Thymus satureioides* in the Ourika region, which it consists of 26.5%, carvacrol, 20.1% of borneol, 8% of camphene, 5.4% of caryophyllene and 3.8% of linalool. Both samples contain carvacrol and borneol as major components. Another study was carried out in the Ifrane region (Middle Atlas) on the essential oil of *T. satureioides*, which represents as major components 27.59% of cymene and 14.09% of thymol [23], this last component was not identified in essential oil of our plant.

This difference in composition is probably due to various conditions including environment, genotype, geographical origin, harvest period, location of drying, temperature, drying time, parasites and extraction method [24, 25].

Table 1. Chemical composition of *Thymus satureioides* essential oil.

Constituents	Kovat's Index	EOFT (%)
Monoterpenes hydrocarbons		
Tricyclene	928	0.28
α -Pinene	950	4.55
Camphene	960	7.01
Sabinene	976	1.07
β -Pinene	980	1.35
3-Carene	1016	1.58
<i>p</i> -Cymene	1026	8.53
γ -Terpinene	1062	6.10
Monoterpenes oxygenated		
α -Thujene	938	1.41
3-Octanol	994	0.21
1,8-Cineol	1033	0.78

Constituents	Kovat's Index	EOFT (%)
Linalol	1098	11.79
Borneol	1166	19.04
Terpineol-4	1178	1.81
<i>Cis</i> -Dihydrocarvone	1194	0.16
Bornyl acetate	1286	0.45
Carvacrol	1299	29.65
Sesquiterpenes hydrocarbons		
α -Copaene	1377	0.06
α -Guaiene	1440	0.05
Caryophyllene	1419	2.39
Aromadendrene	1440	0.05
α -Patchoulene	1456	0.11
Germacrene D	1480	0.03
α -Muurolene	1499	0.15
γ -cadinene	1513	0.07
δ -cadinene	1524	0.22
Sesquiterpenes oxygenated		
Spathulenol	1576	0.07
Caryophyllene oxide	1581	0.13
Cadinol	1653	0.14
Monoterpenes oxygenated		65.39
Monoterpenes hydrocarbons		30.47
Sesquiterpenes hydrocarbons		3.13
Sesquiterpenes oxygenated		0.34
Total identified compounds		99.33

3.2. Weight loss test

3.2.1. Inhibitor concentration effect

The samples are immersed in hydrochloric solution without and with addition of EO at specified inhibitor concentrations (0.05, 0.1, 1.0 and 1.5 g/L). The rate of steel corrosion (*CR*) and inhibitor efficiency (*IE* %) were determined by using the equations 1 and 2 [26], respectively:

$$W = W_b - W_a / At \quad (1)$$

$$IE(\%) = (CR - CR_{inh} / CR) \times 100 \quad (2)$$

Where W_b and W_a are the mass losses before and after immersion in acidic solution; CR , CR_{inh} are the rate of steel corrosion in the absence and presence of EO, respectively. A is the surface area of steel specimen (cm^2) and t (h) is the immersion time.

It can be seen from Table 2 and Figure 1 that the EO acted as a suitable inhibitor of steel corrosion under the investigated conditions. The rate of steel corrosion decreases when the concentration of inhibitor increases, while the values of IE (%) increased with a corresponding increase in the inhibitor concentration. At 1.5 g/L concentration of oil, the inhibition percentage achieved 90%.

Table 2. Results of weight loss method for the corrosion of mild steel in hydrochloric acid at specified concentrations of EO at 303 K.

Inhibitor	Conc.	Corrosion rate ($\text{mg}/\text{cm}^2 \text{ h}$)	Inhibition efficiency (%)	Surface coverage (θ)
Blank	–	1.135	–	–
EO	0.05	0.329	71	0.71
	0.1	0.272	76	0.76
	1.0	0.147	87	0.87
	1.5	0.113	90	0.90

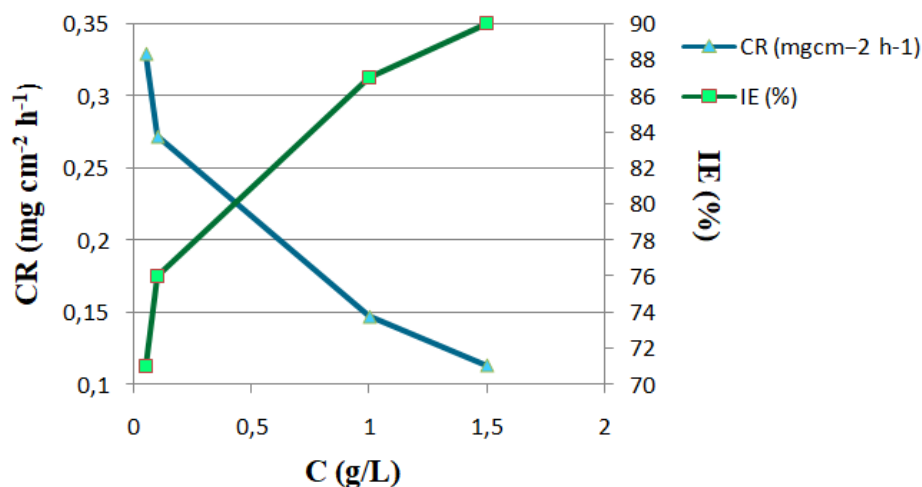


Figure 1. Steel corrosion rate and inhibitor efficiency in HCl medium at varying concentrations of essential oil.

3.2.2. Temperature effect

The temperature is one of the factors that can alter the inhibitors and substrates behavior in a corrosive environment [27]. The higher temperatures promote desorption of inhibitor or its decomposition thus causing a weakening of the corrosion resistance of steel [28]. Weight

loss tests were conducted at different temperatures from 303 to 333 K in order to study the temperature effect on adsorption/desorption processes. Increasing temperature reduces surface covered by the adsorbed inhibitor, which results in a decrease of percentage inhibition efficiency from 89% to 76% (Table 3, Figure 2). This result can be explained by desorption process of inhibitor at high temperature, suggesting physisorption mechanism.

Table 3. Temperature effect on steel corrosion in the absence and presence of 1.5 g/L essential oil.

Inhibitor	Temperature (K)	CR (mg/cm ² h)	IE (%)	Surface coverage (θ)
Blank	303	1.135	—	—
	313	2.466	—	—
	323	5.032	—	—
	333	10.029	—	—
1.5 g/L of EO	303	0.124	89	0.89
	313	0.334	86	0.86
	323	0.965	80	0.80
	333	2.318	76	0.76

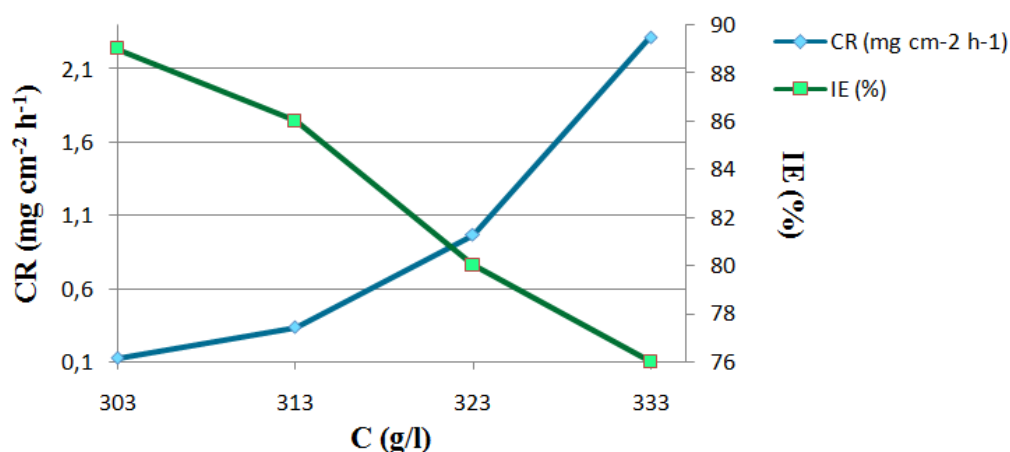


Figure 2. Variation of steel corrosion rate and protection efficiency as a function of temperature.

The Arrhenius plot shown in Figure 3 and the transition state plot (Figure 4) allowed to deduct the activation energy values in uninhibited and inhibited solution, the results are listed in Table 4. The temperature dependency of current density can be best represented by the Arrhenius and transition state equations [29, 30]:

$$CR = k \exp\left(\frac{-E_a^*}{RT}\right) \quad (3)$$

$$CR = \frac{RT}{N\hbar} \exp\left(\frac{\Delta S_a^*}{R}\right) \exp\left(-\frac{\Delta H_a^*}{RT}\right) \quad (4)$$

Where, \hbar is Plank's constant, E_a^* is the apparent activation energy, N is Avogadro's number, ΔS_a^* is the entropy of activation, ΔH_a^* is the enthalpy of activation, R is the gas constant, T is the temperature, k is the Arrhenius pre-exponential factor. These two graphs give a straight line.

In order to understand the nature of adsorption process, the thermodynamic parameters such as activation energy (E_a) standard enthalpy (ΔH), and entropy (ΔS) were calculated. It is clear from Table 4 that E_a value for the corrosion process is higher compared to that obtained in the uninhibited solution. The increased value of the (E_a^*) in the presence of EO could presumably due to the generation of energy barrier for the corrosion reaction in the presence of inhibitor. The same phenomenon was observed during the work of other researchers [31, 32]. The standard enthalpy change (ΔH) can provide valuable information about adsorption process type. Positive value of enthalpy change indicates that adsorption process is endothermic [33]. The reduction in inhibition efficiency ($IE\%$) with increase in temperature and higher E_a value in the inhibitor's presence compared to the blank suggest a physical adsorption mechanism. The effect corresponding to an increase in protection efficiency and the lower value of E_a in inhibited solution to be indicative of chemisorption. In this work, the higher value of activation energy (activated adsorption) shows that the adsorbed inhibitor has created a physical barrier to the charge transfer, leading to reduction in corrosion rate. It is well noticed that the entropy value increases from -98.8 to $-16.86 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. This result can be explained by replacement of water molecule during the adsorption process of essential oil on the substrate surface [34].

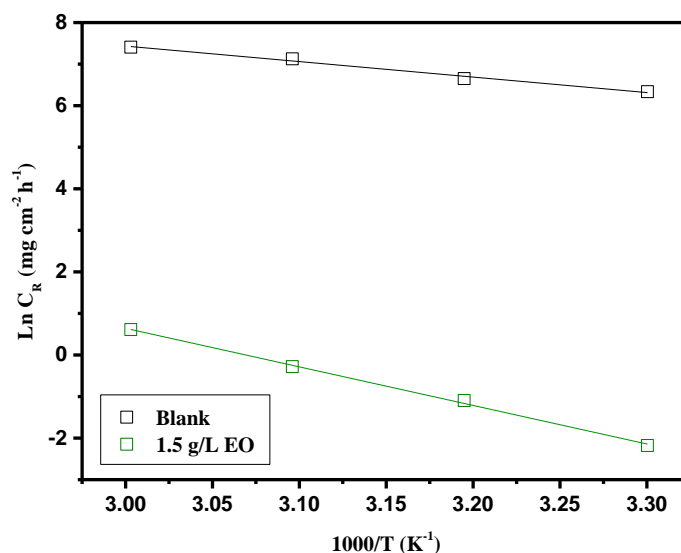


Figure 3. Arrhenius plots of mild steel in absence and presence of 1.5 g/l inhibitor.

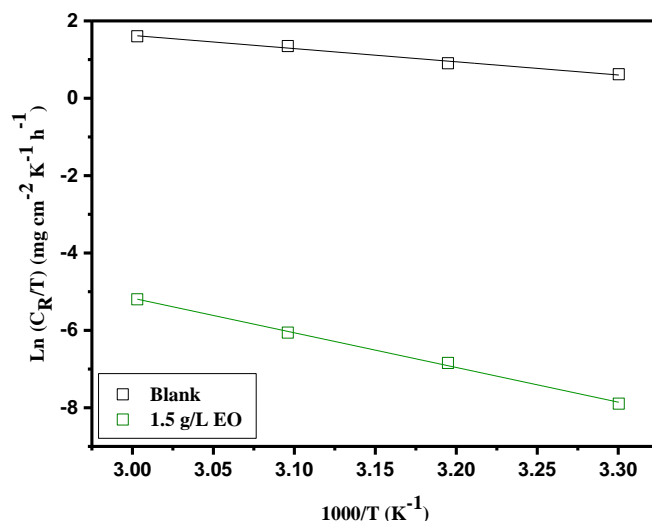


Figure4. Transition state plots (HCl and HCl + 1.5 g/L EO).

Table 4. Activation parameters for the essential oil adsorption onto the steel surface.

Inhibitor	E_a (kJ·mol ⁻¹)	ΔH_{ads} (kJ·mol ⁻¹)	ΔS_{ads} (J/mol·K)	$E_a - \Delta H_a$
Blank	31.00	28.35	-98.8	2.65
1.5 g/l of EO	77.16	74.52	-16.86	2.64

3.3. Polarization curve method

Figure 5 shows the anodic and cathodic polarization curves of steel in hydrochloric medium in the presence and absence of inhibitor. The polarization parameters such corrosion current density (i_{corr}), corrosion potential (E_{corr}), and inhibition efficiency ($IE\%$) for different concentrations of inhibitor are presented in Table 5. The protection efficiency (%) was determined by applying the equation below (5):

$$IE(\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (5)$$

Where i_{corr} and i_{corr}^0 are corrosion current densities in the uninhibited and inhibited acid solutions respectively.

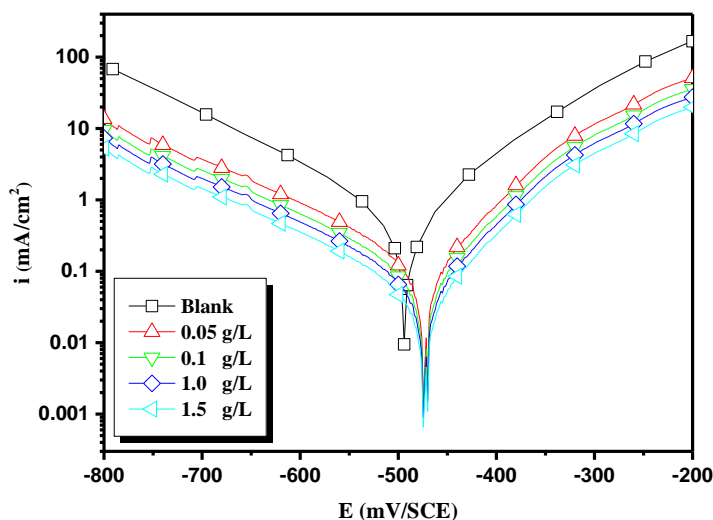


Figure 5. Polarization curves of mild steel in hydrochloric solution for various inhibitor concentrations at 303 K.

Figure 5 shows that the effect of the solution containing inhibitor on the steel presents an anodic and cathodic behavior. The addition of the essential oil in a corrosive medium induces a decrease of the two partial currents cathodic and anodic, reducing of mild steel dissolution and hydrogen evolution reaction in acid solution. The anodic reaction was more effectively than the cathodic reaction of steel. This result indicates that essential oil of the studied plant is a mixed inhibitor with a less predominant anodic effect. The data showed in Table 5 indicate that the inhibitor decreases the corrosion current densities (i_{corr}), meaning that the steel corrosion rate is reduced. After the addition of the inhibitor, the current (i_{corr}) decreases from 153 to 59 $\mu\text{A}/\text{cm}^2$, but the corrosion potential (E_{corr}) remains almost the same. The protection efficiency increased with the inhibitor concentrations to reach 89% at 1.5 g/L. The corrosion protection efficiencies obtained from potentiodynamic polarization curves is in good agreement with results obtained from the gravimetric tests.

Table 5. Polarization measurements of steel in acid medium with specified concentrations of oil at constant temperature (303 K).

Inhibitor	Conc. (g/l)	$-E_{\text{corr}}$ (mV/SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	IE (%)
Blank	—	496.0	564.0	—
EO	0.05	473	153	73
	0.1	474	107	81
	1.0	477	83	85
	1.5	475	59	89

3.4. Impedance measurements study

The addition of the EO as inhibitor on the mild steel corrosion in acid solution was studied by electrochemical impedance spectroscopy measurements at 303 K after 30 minutes of immersion (Figure 6). The results obtained from the Nyquist diagrams are collected in Table 6.

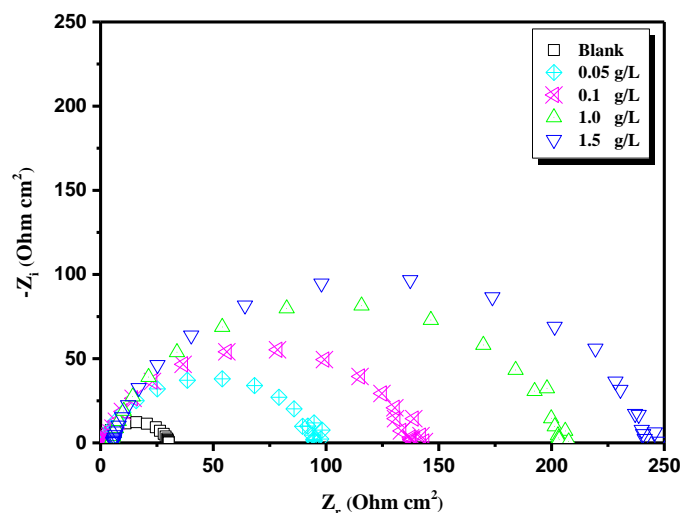


Figure 6. Effect of essential oil concentrations on the Nyquist diagram of mild steel in HCl at constant temperature (303 K).

Table 6: EIS parameters for steel corrosion in HCL in the absence and presence of EO.

Inhibitor	Conc. (g/L)	R_t ($\Omega \cdot \text{cm}^2$)	n	$Q \cdot 10^{-4}$ ($\text{s}^n / \Omega \cdot \text{cm}^2$)	C_d ($\mu\text{F} \cdot \text{cm}^{-2}$)	IE (%)
Blank	—	29.35	0.91	1.7610	91.63	—
EO	0.05	93	0.81	1.1543	40	68
	0.1	135	0.81	0.8911	31	78
	1.0	196	0.86	0.4449	20	85
	1.5	236	0.86	0.3689	17	87

The Nyquist impedance diagram in Figure 7 exhibited a depressed semi-circle indicating a double layer capacitance, this depression (no perfect semi-circle) is may be the result of surface heterogeneous, which results from adsorption of the inhibitor, distribution of the active sites and surface roughness [35, 36], or formation of porous layers [37, 38]. The value of n can be used as a measure of the roughness on the steel surface [39, 40]. We can observe the increase of depressed semi-circle diameter with an increase in inhibitor concentration results from the adsorption of the essential oil on mild steel surface [41] and

formation of a protective layer. The structural model shown in figure 7 was used to analyze the EIS tests. This circuit consists of a constant phase element (Q), used to account for the previously described inhomogeneities, the electrolyte resistance (R_s) and the resistance (R_{ct}). It is by a constant phase element (CPE) that one reports the inhomogeneities of surface by the intermediary of the coefficient n . Such an element is described by:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (6)$$

Where Q is the CPE constant (in $\Omega^{-1} \cdot S^n \cdot cm^{-2}$), ω is the angular frequency (in $rad \cdot s^{-1}$), $j^2 = -1$ is the imaginary number and n is a CPE exponent.

Hirschorn et al recently published that the effective capacity, $C_{dl(eff)}$, can be estimated using the following mathematical formula from the CPE [42]:

$$C_{dl(eff)} = \sqrt[n]{Q \times R_{ct}^{1-n}} \quad (7)$$

Where Q is CPE constant and n is CPE exponent. The value of n represents the deviation from the ideal behavior and it lies between 0 and 1.

The calculated parameters are collected in Table 6. The percentage protection efficiency is determined by the equation (8):

$$IE(\%) = R_t - R_t^0 / R_t \times 100 \quad (8)$$

Where, R_t^0 and R_t were the polarization resistance inclusive and exclusive of inhibitor, respectively.

It is apparent from Table 6 that the impedance of the inhibited system amplified with the inhibitor and the C_d values decreased with inhibitor. This decrease in C_d results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that EO molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface [10]. The impedance study confirms the inhibiting characters of the investigated inhibitor obtained with potentiostatic polarization and gravimetric methods. These observations show that the EO molecules are adsorbed on the mild steel surface. Thus, the investigated inhibitor can be used effectively to protect mild steel in acidic mediums.

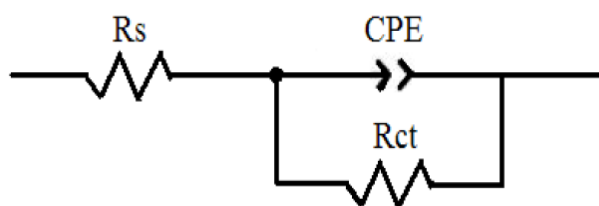


Figure 7. Equivalent electrical circuit of the electrochemical impedance spectra.
CPE: constant phase element, R_s : electrolyte resistance, R_{ct} : charge transfer resistance.

4. Conclusion

We can conclude from this study:

1. The major constituents of essential oil were carvacrol (29.65%), followed by borneol (19.04%), linalool (11.79%), *p*-cymene (8.53%), camphene (7.01%), γ -terpinene (6.10%), α -pinene (4.55%) and caryophyllene (2.39%).
2. Good effectiveness of *Thymus satureioides* essential oil on steel corrosion in hydrochloric medium. The percentage protection efficiency achieved 89% at inhibitor concentration 1.5 g/L.
3. Essential oil is a mixed inhibitor with a predominant anodic inhibition.
4. The value of enthalpy is positive, which indicated endothermic adsorption process.
5. The inhibition efficiencies calculated by weight loss exhibit a trend parallel to that of polarization and electrochemical impedance spectra measurements.

Acknowledgements

A. Boukhraz is grateful to Dr. Hassane Lgaz, Konkuk University, South Korea for the support of this research.

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