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Effect of Thyme Leaves Hydroalcoholic Extract on Corrosion Behavior of API 5L Carbon Steel in 0.5 M H_2SO_4

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Abstract- In this study, the effect of Thyme leaves hydroalcoholic extract **(**as a green corrosion inhibitor) on corrosion behavior of API 5L carbon steel in 0.5 M H_2SO_4 solution was investigated by Tafel polarization and electrochemical impedance spectroscopy (EIS). Tafel polarization plots showed that Thyme is a mixed inhibitor. Also, Tafel polarization and EIS results indicated that the inhibition efficiency increases with increasing Thyme leaves hydroalcoholic extract concentration to attain 89% at 12 g/L. Impedance parameters change with increasing concentration of extract shows that the adsorption of this extract on the steel surface will form a protective layer on the steel surface. Moreover, Temkin isotherm revealed that Thyme physically is absorbed on API 5L carbon steel surface in 0.5 M H_2SO_4 solution. The adsorption isotherm was obtained -17.86 kJ mol^{-1}.

Keywords- API 5L carbon steel, Thyme Extract, Polarization, EIS, Temkin isotherm

1. INTRODUCTION

In general, acid solutions are employed to remove undesirable level and rust in many industrial processes. Hydrochloric acid and sulfuric acids are used extensively in the pickling actions of metals [1]. Corrosion damage can be prevented using a variety of methods including upgrading materials, composition of production fluids, process control, and chemical inhibitors [2,3]. One of the best and most efficient ways to tackle corrosion damage is the use of corrosion inhibitors [4]. In this regard, organic compounds which contain nitrogen, sulfur, and oxygen are the most commonly used inhibitors encountering acid media [5].

A number of synthetic compounds are known to be applicable as desirable corrosion inhibitors for metals. However, due to strict environmental regulations and toxic effects of synthetic compounds to the lives of humans and animals, the popularity and the use of synthetic compounds as corrosion inhibitors are reducing. Consequently, researchers are actively seeking corrosion inhibitors with low toxicity and acceptable performance [2,6]. Recently, research in the field of ‘‘green’’ or ‘‘eco-friendly’’ corrosion inhibitors has been dealing with the goal of harnessing effective cheap compounds associated with a low to zero impact on the environment [7].

Surprisingly, some types of plant extracts have found their way into the realm of corrosion inhibitors. The use of natural products as corrosion inhibitors can be traced back to the 1930 s when plant extracts of Chelidonium majus (Celandine) and other plants were used in H_2SO_4 pickling baths for the first time [8]. These types of inhibitors are classified as eco-friendly and they can be obtained from natural products such as plant extracts [9]. Inexpensive, non-toxic, easy production and availability of green corrosion inhibitors has led many researchers to turn towards them. Recently, several studies have carried out on the corrosion inhibition of metals by means of plant extracts [10], essential oils [11] or purified compounds [12]. Due to the high efficiency and compatibility with the environment, these inhibitors could be a good replacement for conventional corrosion inhibitors [7].

A member of the Lamiaceae family named Thyme (Thymus vulgaris) is an aromatic herb which has medicinal properties. Although it is native to the Mediterranean region of Europe, it is also widely cultivated in Iran. In addition, Thyme contains recognized initial compounds such as essential oils, saponins, acid triterpenes, tannins, and flavonoids. Thyme extract exhibits anti-oxidative, anti-mycotic, anti-bacterial properties. Moreover, it can be used as a natural food preservative and an agent in order to delay the aging of mammals [13].

Thymes vulgar L. plant extract, commonly known as Thyme, has proven to be an effective corrosion inhibitor for mild steel in HCL [14], 1 M HNO_3 [15], NaCl [16], with the aid of different electrochemical techniques and inhibition efficiency maximum respectively 84, 94 and 90% were reported. Following these positive results, we examined Thyme extract as a corrosion inhibitor in a solution of sulfuric acid. The main purpose of this study is to review the action of Thyme leaves hydroalcoholic extract as a non-toxic corrosion inhibitor for API 5L carbon steel in 0.5 M H_2SO_4 solution using various electrochemical techniques. Also, the surface morphology of this steel was studied by scanning electron microscope and optical microscope.

2. MATERIALS AND METHODE

2.1. Preparation of Thyme Extract

The preparation of the test solution is as follows. First, 9 g of the plant extract was added to 250 ml of water-ethanol mixture (4:1 v/v) and it was stirred at 150 rpm and 25°C for 3600 s. Next, the solution was filtered out through Filter paper. Then, the resulting solution was dried in a rotary evaporator at 35°C. After that, the resulting powder was placed in a freeze dryer in order to be lyophilized. Finally, the freeze dried powder was redistributed in the ethanol-water mixture to obtain the desirable test solution.

2.2. Electrochemical Measurements

The chemical composition of API 5L carbon steel used in this experiment is shown in Table 1. All samples were polished to 1200 grit and cleaned with distilled water prior to each test. Three electrodes cell were used for electrochemical tests. Saturated calomel electrode as a reference and a platinum electrode as auxiliary electrode were used. API 5L carbon steel with an area of 0.4 cm^2 was utilized as the working electrode.

Table 1. Chemical composition of API 5L carbon steel

	C	**Mn**	**P**	**Ti**	**Fe**
API 5L Carbon Steel/ wt%	0.28	1.20	0.30	0.04	Bal

Prior to the electrochemical tests, the cell was filled with 250 ml 0.5 M H_2SO_4 solution. In order to achieve a steady state condition, immersion of the working electrode in 0.5 M H_2SO_4 solution was performed for 1800 s. With the sweep rate of 1 mV/s and the range -0.25 to +0.25 V rather than the corrosion potential, Tafel polarization was done. EIS tests were recorded over the frequency range 100 kHz to 10 mHz and with a 10 mV amplitude. NOVA software was used for modeling the EIS data.

2.3. Investigation of Corrosion Attack Morphology

To examine the corrosion attack morphology in the presence and absence of inhibitors, scanning electron microscope and optical microscope were used. Polished samples with 0.05 μm alumina slurry were placed in the acidic solution with and without inhibitor (12 g/L) for 1800 s at 25°C.

3. RESULTA AND DISCUSSION

3.1. Electrochemical Measurements

Tafel polarization curves of API 5L carbon steel samples in the presence and absence of Thyme in 0.5 M H_2SO_4 are shown in Fig. 1. The passive area is not clearly defined for two reasons: either non-protective film is formed or there are impurities in steel [16]. Obtained corrosion parameters of the curve can be seen in Table 2. These include corrosion potential (E_{corr}), corrosion current density (i_{corr}), and cathodic Tafel slope (B_c). It can be observed that corrosion current density is reduced in the presence of Thyme extract. Moreover, by increasing the concentration of the extract, corrosion current density is diminished. Table 2 indicates that the presence or absence of inhibitor does not change the corrosion potential drastically. Therefore, Thyme can be considered as a mixed type inhibitor [17]. The inhibition efficiency (η) can be calculated using Eq. (1) [14]:

$$\eta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \qquad (1)$$

Where i_{corr} is the value of corrosion current density in the presence of the inhibitor and i^0_{corr} is the value of corrosion current density in the absence of the inhibitor.

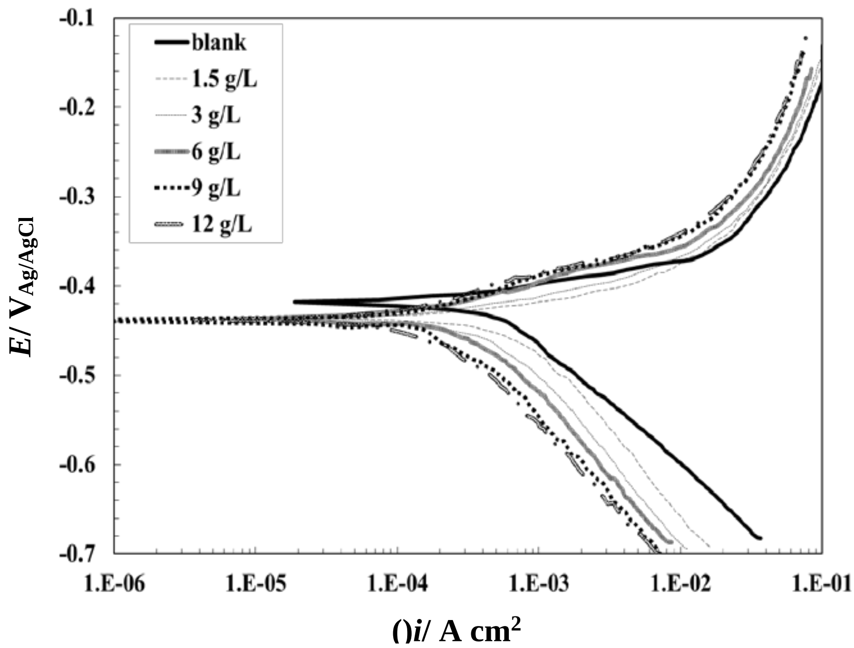

Fig. 1. Tafel polarization curves of API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentration of Thyme leaves extract.

Table 2 also indicates that the inhibition efficiency increases with increasing the concentration of Thyme. It reaches its maximum value of 75.03 in acid media when the extract concentration is 12 g/L in H_2SO_4. These results are in close agreement with those obtained from the EIS measurements.

Table 2. Electrochemical parameters derived from Tafel plots of API 5L carbon steel sample immersed in 0.5 M H_2SO_4 with and without Thyme extract inhibitor

C_{Thyme} (g/L)	i_{corr} (μA/cm^2)	E_{corr} (mV)	β_c (mV/decade)	η (%)
0	424.2	418.3	133.3	-
1.5	295.1	434.9	34.5	30.44
3	218.5	435.4	48.6	48.47
6	174.4	436.5	95.6	58.87
9	130.8	438.0	125.0	69.26
12	105. 9	438.2	120.1	75.03

In an attempt to describe the capacitive behavior of Thyme leaves extract on the corrosion behavior of API 5L carbon steel, EIS measurements were carried out. Fig. 2 indicates the Nyquist plots with and without Thyme leaves extract addition in 0.5 M H_2SO_4 solution.

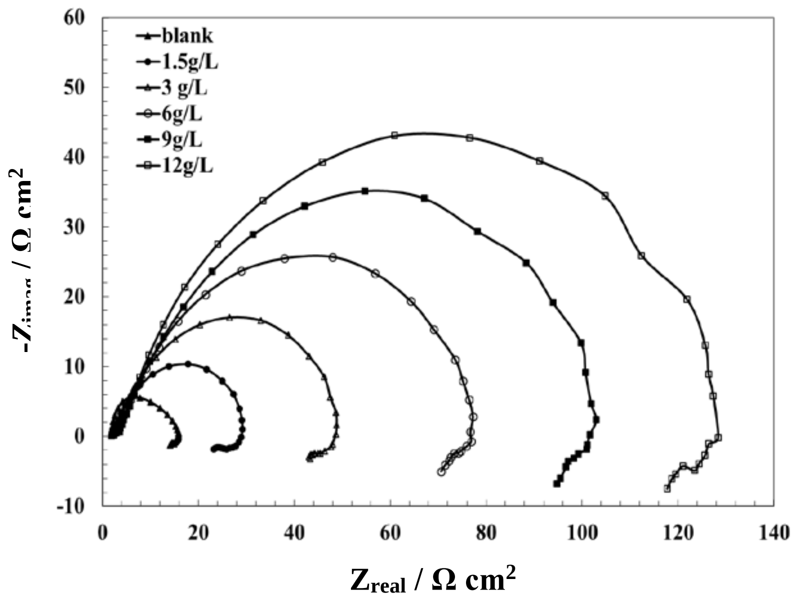

Fig. 2. Nyquist plots of API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentration of Thyme leaves extract

Nyquist curves are semi-circles and consist of one time constant. These curves consist of a large capacitance loop (double-layer capacitance) and induction loop in the applied frequency range. The induction loop is caused by absorbing ions such as H^+_{ads} and SO_4^{2-} [18].

The equivalent circuit which is shown in Fig. 3 was used for the analysis of impedance data. In this equivalent model, R_s is the solution resistance, R_{ct} is the charge transfer resistance, *CPE* shows the constant phase element [19-22], and *L* and R_L represent the additional inductive elements.

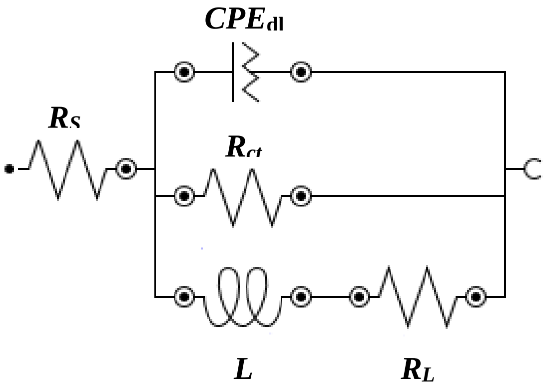

Fig. 3. The best equivalent circuit used to model the experimental EIS data of API 5 L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentration of Thyme

The similar impedance curves indicated that the added Thyme extract in H_2SO_4 solution had no effect on corrosion mechanism as shown in Fig. 2. However, the diameter of the semi-circle increased as the extract concentration increased from of 1.5 g/L to 12 g/L. Electrochemical parameters consist of solution resistance, charge transfer resistance, double layer capacitance, inductive elements and inhibition efficiency (η) were listed in Table 3. Inhibition efficiency is dependent on the concentration of extract and with increasing the concentration of the extract, the inhibition efficiency increases. The inhibition efficiency can be calculated from EIS data using Eq. (2) [14]:

$$\eta = \frac{R_{ct} - R_{ct}^{0}}{R_{ct}} \tag{2}$$

Where R_{ct} and R_{ct}° are the charge transfer resistance in the presence and absence of Thyme, respectively. The transfer function according to a simple Faradaic reaction without diffusion under the influence of the *CPE* was expressed for showing the proportional to the capacitance while that is obviously not an ideal capacitance (n<1). The reason for *CPE* behavior in an electrode is independent of frequency and explained by a phase angle maxima less than 90° [23]. It must be mentioned that for a circuit including a *CPE*, C_{dl} can be calculated from Eq. (3) [23]:

$$C_{dl} = Y_{0dl}\left(\omega_{\max}\right)^{n} \tag{3}$$

Where C_{dl} is the double layer capacitance, Y_{0dl} is the admittance of the double layer, ω_{max} is the angular frequency at which the imaginary part of the impedance has a maximum, *n* is a parameter related to surface roughness.

Table 3. Electrochemical parameters derived from EIS plots of API 5 L carbon steel sample immersed in 0.5 M H_2SO_4 with and without Thyme extract inhibitor

C_{Thyme} (g/L)	R_S (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	*L* (H)	R_L (Ω cm^2)	Θ	η (%)
0	1.80	14.0	131.9	322.49	84.06	-	-
1.5	2.13	28.03	106.9	66.01	110.12	0.50	50.05
3	2.29	48.66	80.4	198.14	260.92	0.71	71.22
6	2.79	77.99	63.7	596.04	583.92	0.82	82.04
9	3.25	104.86	60.3	851.37	795.75	0.87	86.64
12	3.31	130.23	59.3	1101.0	1029.90	0.89	89.24

The values of double layer capacitance (C_{dl}) were seen to decline with increasing the concentration of extract into the acid media. Double layer capacitance decrease is due to the increase in the thickness of the double layer that move water molecules adsorbed on the API 5L carbon steel surface leads to, extract these molecules are replaced, as a result the dielectric constant is decreased [24]. As a result, API 5L carbon steel surface will be protected against acid attack. Helmholtz model also addresses this subject in other words which consider the dielectric constant of the medium, the thickness of the protective layer, the exposed area, and the vacuum permittivity [25].

3.2. Adsorption Mechanism of Corrosion Inhibition

Many organic inhibitors have polar groups that have at least a sulfur, nitrogen, selenium, or sometimes a phosphorus atom. Electron density affects inhibitory properties of organic compounds [26]. Strong chemisorption between inhibitor and metal surface can be caused by an increase in electron density [27,28]. The plant Thyme extract is made up of several natural organic compounds. As a result, absorption of these compounds on the surface of the steel causes inhibition.

To obtain useful information about absorption, an adsorption isotherm can be used parallel to the EIS analysis. Langmuir isotherm is a well-known model that can be adopted initially. Fig. 4 shows the curve obtained based on the ratio of extracts concentration (*C*) to the surface coverage (θ). Straight line graphs were obtained with a line slope (R^2) in 0.5 M H_2SO_4 solution. Langmuir isotherm can be expressed using Eq. (4) [14]:

$$\frac{C}{\theta}=\frac{1}{K}+C \quad (4)$$

Where C is the concentration, θ is the surface coverage, and K_{ads} is the equilibrium constant in the absorption process. Gibbs free energy (ΔG^0_{ads}) is calculated by Eq. (5) [14]:

$$\Delta G^0_{ads} = -RT\ln(55.5\times K) \quad (5)$$

Where R shows the molar gas constant, T represents the temperature in Kelvin, and 55.5 is the concentration of water in mol dm^{-3}.

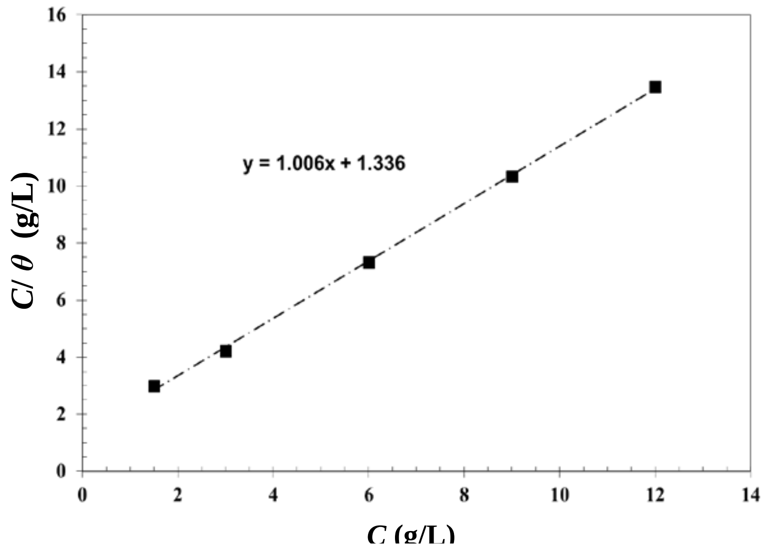

Fig. 4. Langmuir adsorption isotherm for API 5L carbon steel in the absence and presence of Thyme leaves extract in 0.5 M H_2SO_4

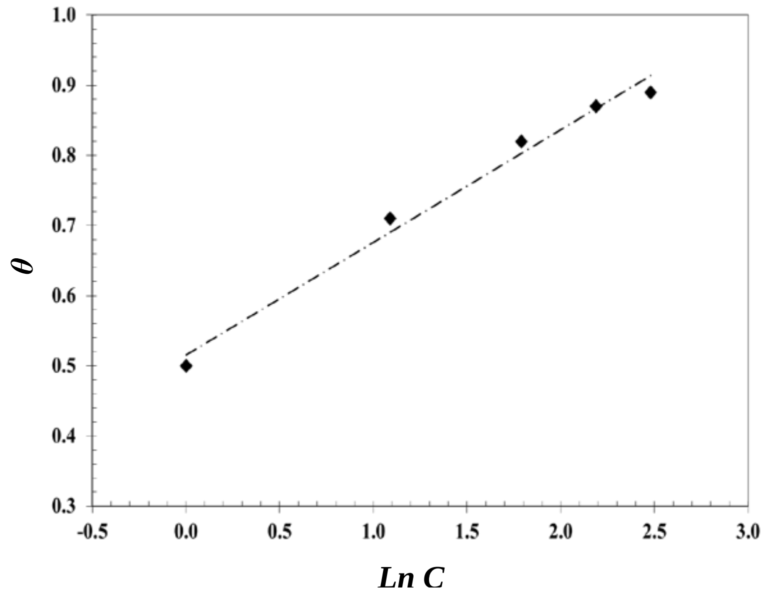

Fig. 5. Temkin Langmuir adsorption isotherm for API 5L carbon steel in the absence and presence of Thyme leaves extract in 0.5 M H_2SO_4

On the other hand, Temkin isotherm is similar to the Langmuir isotherm. This is also a well-established model for the interaction between adsorbed species and it is obtained by Eq. (6) [14]:

$$\theta = \frac{1}{2a}\ln k + \frac{1}{2a}\ln C \tag{6}$$

In this equation, K is the adsorption– desorption equilibrium constant and a shows the lateral interaction term. A linear relationship was found to exist between θ and 1nC with a slope of 0.16 in 0.5 M H_2SO_4 solution which contains different concentrations of the Thyme extract, as it is exhibited in Fig. 5. The absorption parameters obtained from Temkin isotherm plot are shown in Table 4. Positive values indicate lateral forces between the molecules that are absorbed in the absorption layer [29].

Table 4. Adsorbtion isotherms for Thyme leaves extract in 0.5 M H_2SO_4 solution on API 5L carbon steel

	R^2	K_{ads}	ΔG^0_{ads}	A
Isotherms Langmuir	1.00	0.74	-10696	-
Isotherms Temkin	0.16	24.44	-17869	3.11

Stability of the adsorbed layer can be understood by the negative value of ΔG^0_{ads}. The calculated value of ΔG^0_{ads} was -17.86 kJ mol^{-1} which showed that Thyme was absorbed physically. In general, when ΔG^0_{ads} absolute value is equal to 20 kJ mol^{-1} or less, physical adsorption due to electrostatic forces between the extract and the steel surface will occur. If the ΔG^0_{ads} absolute value is greater than 40, Chemisorption will occur [30,31].

3.3. Corrosion Attack Morphology

Using a scanning electron microscope and optical microscope, the surface morphology of API 5L carbon steel samples immersed in 0.5 M H_2SO_4 solution with and without inhibitor for 1800 s were studied .in Fig. 6a. API 5L carbon steel polished surface placed in the blank solution was highly corroded in 0.5 M H_2SO_4 (Fig. 6b and Fig. 7a) While the corrosion attack was not discernible in the solution which contained inhibitor (Fig. 6c and Fig. 7b). These observations are also in conformity with the obtained electrochemical results [1].

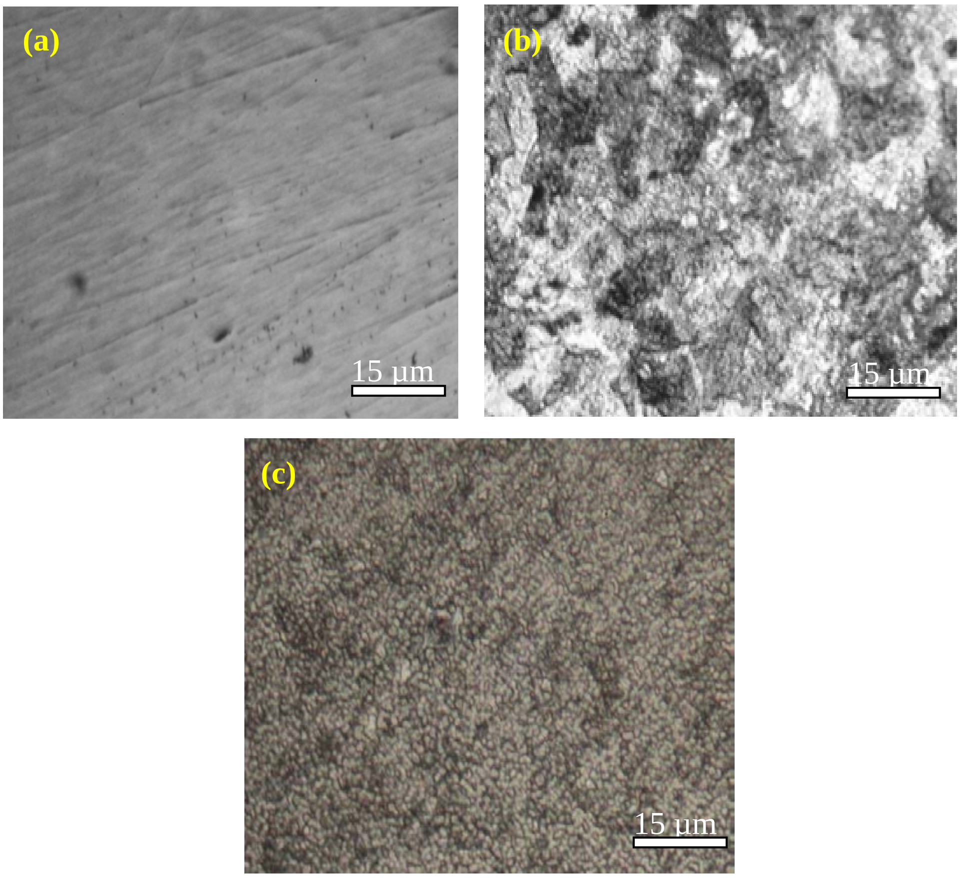

Fig. 6. Optical microscopy images of API 5L carbon steel, (a) before immersion, (b) after immersion (1800 s) in 0.5 M H_2SO_4, and (c) after immersion (1800 s) in 0.5 M H_2SO_4+12 g/L Thyme leaves extract

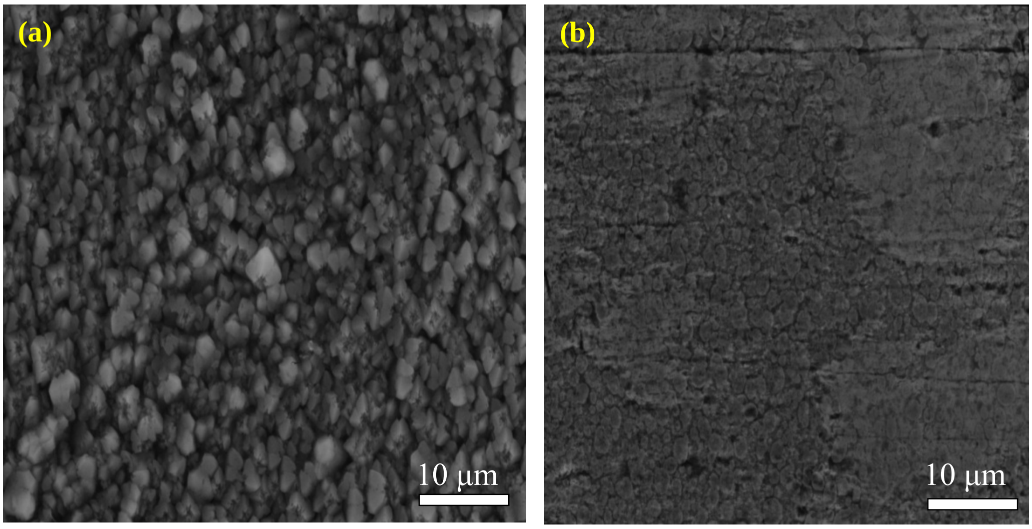

Fig. 7. Scanning electron microscope images of API 5L carbon steel, (a) after immersion (1800 s) in 0.5 M H_2SO_4, and (b) after immersion (1800 s) in 0.5 M H_2SO_4 + 12 g/L Thyme leaves extract

4. CONCLUSIONS

Effect of Thyme leaves extract (as a green corrosion inhibitor) on corrosion behavior of API 5L carbon steel in 0.5 M H_2SO_4 solution was studied. The results showed that Thyme leaves extract has a significant effect on reducing the rate of corrosion of API 5L carbon steel in 0.5 M H_2SO_4 solution. Also, the results revealed that Thyme leaves extract acts as a mixed type inhibitor. Absorption of this inhibitor on API 5L carbon steel surface follows from Temkin isotherm. The obtained value of ΔG_{ads}^{0} indicated that adsorption of the present inhibitor on API 5L carbon steel surface was physical. Finally, scanning electron microscope and optical microscope images showed that Thyme leaves hydroalcoholic extract acts as an inhibitor for API 5L carbon steel corrosion in 0.5 M H_2SO_4 solution.

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