Anal. Bioanal. Electrochem., Vol. 14, No. 4, 2022, 362-373

Analytical &
Bioanalytical
Electrochemistry

2022 by CEE
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Full Paper

Electrochemical And Corrosion Behaviors of Commercially Pure Titanium (CP-Ti) In 3.0 Wt.% Nacl Solution Containing a Green Corrosion Inhibitor

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Received: 19 October 2021 / Received in revised form: 12 April 2022

Accepted: 13 April 2022 / Published online: 30 April 2022

Abstract- The object of this work is to evaluate the inhibitory efficiency of the essential oil of leaves of *Pistacia lentiscus* (EOPL) on the corrosion of commercially pure titanium (CP-Ti) in a simulated marine environment (3.0 wt. % NaCl). The inhibition effectiveness of this green corrosion inhibitor was investigated using weight loss measurement and potentiodynamic polarization in the presence of different concentrations of EOPL ranging from 0.1 to 2.0 g/L. A complementary vision of this study is obtained by means of surface characterization by scanning electron microscopy (SEM). Adsorption of the inhibitor on the titanium surface obeyed Langmuir's isotherm. The thermodynamic parameters were determined and discussed. It is found that the activation energy increases with an increase in inhibitor concentration, suggesting physisorption. With increasing EOPL concentration, inhibition increased to 84.58% at 2.0 g/L. Thus, the results obtained from the different techniques used in this work are in very good agreement and revealed that EOPL of *Pistacia lentiscus* could be used as a source of green corrosion inhibitors on CP-Ti in 3.0 wt. % NaCl solution.

Keywords- Corrosion inhibition; Green inhibitor; Titanium; Electrochemical measurements; Adsorption isotherm

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1. INTRODUCTION

Titanium and its alloys are widely used; they have a good compromise between their mechanical properties and their densities. The characteristics of titanium allow it to be used in the seawater environment for heat exchangers in seaside nuclear power plants, seawater desalination plants, and, more generally, for on-board equipment on boats and off-platforms. Consequently, the risks of corrosion appear in these environments. The excellent corrosion resistance of titanium alloy results from the stable and compact oxidation film [1-4]. A thin oxidation film can spontaneously and rapidly form on its surface, which will protect the titanium alloy from corrosion. Due to the very small thickness of the oxidation film, it is very easy for the titanium alloy to be damaged when it contacts the other components. In this case, the exposed surface will act as a sacrificial anode for the shield of the oxidation film, which will accelerate the corrosion of titanium alloy. On the other hand, the oxidation film is also easy to peel off due to its weak bonding with titanium alloy. As a result, the exposed surface will act as a sacrificial anode for protection of the oxidation film, which will accelerate the corrosion of titanium alloy. In addition, the oxidation film can also be dissolved, especially in Cl^- concentrate solution, due to the competitive adsorption between Cl and O ions. Those phenomena will limit the application and reduce the life of titanium alloy.

Corrosion has not only economic implications, but it contributes significantly to environmental pollution [5-10]. Because of these effects, corrosion is an undesirable phenomenon that ought to be prevented. Several methods available can be employed to slow or prevent corrosion of metallic structures, but the application of inhibitors has been proven to be the most practical and efficient for this purpose [11].

Corrosion inhibitors are substances that, when added in low concentrations to corrosive media, decrease or prevent the reaction of the metal with its environment. The use of inhibitors to prevent the dissolution process of metals remains an inevitable and widespread application. The majority of synthetic inhibitors show good anti-corrosion action, but most of them are highly toxic to humans and the environment. These inhibitors can cause temporary or permanent damage to organ systems such as kidneys or liver, or disrupt the enzyme system in the human body. Recently, due to environmental concerns, essential oils and plants extract are increasingly seen as a source of green corrosion inhibitors. They are used for the protection of metals in the saline environment in order to replace the toxic chemicals currently used.

The objective of this work is to study the inhibition of titanium corrosion by the essential oil of *Pistacia lentiscus* in a saline medium (3.0 wt. % NaCl). Corrosion inhibition has been studied using mass loss, and potentiodynamic polarization techniques. Adsorption isotherm was investigated to characterize the adsorption behavior on the surface of titanium (CP-Ti). The surface morphology of the CP-Ti samples before and after corrosion experiments was examined using scanning electron microscopy (SEM).

2. EXPERIMENTAL STUDIES

2.1. Materials and preparation of test solutions

The working electrode is prepared from commercially pure titanium (grade 4). All test samples were cut to the dimensions of 15×10×1.2 mm. The chemical composition of the titanium plate is shown in Table 1.

Table 1. The chemical composition of CP-Ti plate

CP-Ti substrate					
Element	Fe	O	C	H	N
%composition by weight	<0.25	<0.15	<0.08	<0.012	<0.06

Before use, the exposed surfaces were mechanically polished with grade 1200 SiC abrasive paper, rinsed with distilled water, then degreased with acetone and finally dried before each experiment.

The aggressive solution, 3.0 wt.% NaCl (simulated atmospheric marine environment), was prepared by the dilution of 3.0 g of salt with 100 g of distilled water.

2.2. Inhibitor preparation

The tested inhibitor in this study is the essential oil of *Pistacia lentiscus*, which was obtained from the leaves using a Clevenger-type apparatus. Then, the essential oil is kept at a temperature of 273 K away from light until the preparation of the working solution.

2.3. Electrochemical tests

Electrochemical test experiments were conducted with a potentiostat (273A EG&G PAR) combined with “Power Suite Software”. The potential ranged from -900 to +1000 mV/Ag/AgCl with a speed of 1.0 V/s. The electrochemical measurement was carried out with a conventional three-electrode electrochemical cell. The platinum was used as an auxiliary electrode, the saturated calomel electrode (SCE) as a reference electrode, while the commercially pure titanium (CP-Ti) was utilized as the working electrode. The working size exposed to the corrosive solution was 1 cm^2.

2.4. Weight loss experiments

Weight loss measurements were carried out according to the standard methods [12,13]. Samples used with dimensions of 15×10×1.2 mm were abraded with a series of emery papers SiC to 1200 grade, and then they were washed with double distilled water, degreased, and dried with acetone. The inhibitor was tested at different concentrations. The weight of each sample was measured before and after the aggressive solution test, with a high precision analytical balance. The CP-Ti samples are cleaned, dried, and weighed, then immersed in 500 ml of a 3.0 wt% NaCl solution with different concentrations of EOPL at 298 K for 24 hours. After the immersion period, the samples of CP-Ti were washed, dried, and weighted again by analytical balance.

2. 5. Surface characterization

The surface morphology of the CP-Ti in 3.0 wt% NaCl solution without and with different concentrations of inhibitor before and after corrosion experiments was examined by means of a JEOL JSM 6400F scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization technique

Polarization tests were carried out in order to investigate the inhibition efficiency of the essential oil of *Pistacia lentiscus* (EOPL) against titanium corrosion in 3.0 wt.% NaCl solution. The polarization curves for the titanium electrode in the absence and presence of an inhibitor in a 3.0 wt.% NaCl solution at 298 K are presented in Figure 1. The relevant corrosive parameters, such as corrosion current density (i_{corr}) and corrosion potential (E_{corr}), which are obtained by extrapolation of the Tafel lines, are summarized in Table 2.

Table 2. Corrosion potential (E_{corr}) and current density (i_{corr}) for CP-Ti in 3.0 wt.% NaCl solution in the absence and the presence of EOPL at 298 K

EOPL concentration g/L	E_{corr} (V/SCE)	i_{corr} (µA/cm^2)
0	-0.450	1.016
0.5	-0.460	0.897
1.0	-0.393	0.853
2.0	-0.237	0.797

It can be seen that the electrochemical reactions at the metal electrolyte interface are inhibited in the presence of these molecules. Thus, the addition of those inhibitor molecules reduces the CP-Ti dissolution and retards the hydrogen evolution reaction [14,15].

With introducing the EOPL in 3.0 wt.% NaCl solution, the value of the E_{corr} for CP-Ti was more positive compared with the uninhibited solution (Figure 1). Figure 2 illustrates the corrosion potential (E_{corr}) as a function of time for CP-Ti in 3.0 wt.% NaCl without and in the presence of inhibitor (EOPL). It can be observed that the adsorption of EOPL on the CP-Ti surface gives rise to a decrease in the current density compared to that of the blank (3.0 wt.% NaCl solution). This effect is attributed to the modification of the reaction process owing to the surface of the electrode which is coated by a protective film, due to the blocking of active sites. This film appears to inhibit the electrochemical reactions effectively. It can be concluded that the EOPL adsorbs on the sites of the CP-Ti surface [16].

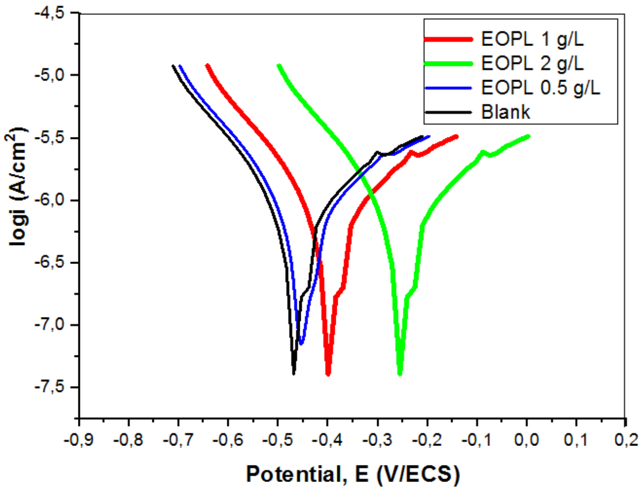

Figure 1. Tafel curves of CP-Ti in 3.0 wt.% NaCl solution in the absence and presence of EOPL with various concentrations at 298K

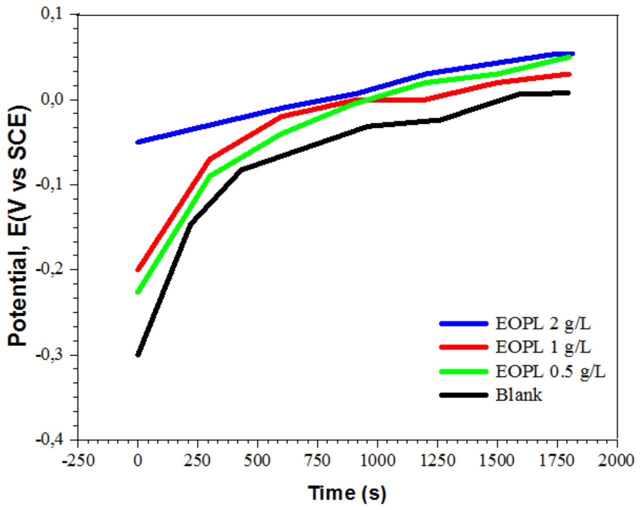

Figure 2. The variation of corrosion potential with time of CP-Ti in a 3.0 wt.% NaCl solution containing different concentrations of EOPL with different concentrations at 298K

3.2. Weight loss tests

Weight loss measurements are the simplest way of calculating the corrosion rate of the metal. It consists of exposing the sample to the test medium such as seawater (3.0% by weight of NaCl) and measuring the weight loss of the material as a function of time, E_{wL}% signifies corrosion inhibitor efficiency [17].

$$E_{WL}\% = \frac{w_0 - w_i}{w_0} \times 100 \qquad (1)$$

Corrosion rates C_R were calculated by following equation:

$$C_R = (W_0 - W_i)/(A.t) \qquad (2)$$

where W_0 and W_i are the weights of CP-Ti specimens before and after immersion in corrosive solution, respectively, A is the surface area of the tested specimens, and t is the immersion time. The degree of surface coverage (θ) on the metal surface is equal to E_{wL} /100 and is calculated using equation 3.

$$\theta = \frac{w_0 - w_i}{w_0} \qquad (3)$$

The values of the inhibition efficiency (E_{wL}%) and corrosion rate (C_R) with different concentrations of EOPL in 3.0 wt.% NaCl solution at 298 K are shown in Table 3.

It is clear that the corrosion rate markedly decreased, and that the inhibition efficiency increased with an increasing inhibitor concentration. Table 3 shows that the maximum value of E_{wL} is 84.58 % at 2.0 g/L, which indicates that the essential oil of *Pistacia lentiscus* acts as a good inhibitor for CP-Ti in 3.0 wt.% NaCl. This behavior is due to the fact that the adsorption amount and coverage of inhibitor on the titanium surface increase with the inhibitor concentration. The inhibition action of EOPL acts as a barrier between the titanium surface and the aggressive solution, leading to a decrease in the corrosion rate.

Table 3. Corrosion parameters data obtained from weight loss measurements of CP-Ti in 3.0 wt.% NaCl containing different concentrations of EOPL after 24 hours of immersion at 298K

C_{inh} (g/L)	Δw (g)	$C_R .10^{-5}$ ($g.cm^{-2} .h^{-1}$)	E_{wL} (%)	θ
0	0.009	2.3794	_	_
0.1	0.005	1.8339	22.92	0.22
0.5	0.0025	0.7704	67.62	0.67
1	0.0022	0.5816	75.55	0.75
1.5	0.0014	0.4935	79.25	0.79
2	0.0010	0.3667	84.58	0.84

3.3. Adsorption isotherm

The interaction between the inhibitor molecules and the CP-Ti surface can be understood from the adsorption isotherm [18]. Langmuir's adsorption isotherm was found to be the most frequently used adsorption isotherm, which can provide the best description of the adsorption of the investigated inhibitors [19,20]. The Langmuir isotherm follows equation 4 [21]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{4}$$

where C_{inh} the inhibitor concentration, K_{ads} is the constant balance of the adsorption-desorption process. The linear regression coefficient, R, was used as a criterion to select the suitable adsorption isotherm.

The primary step in the action of inhibitors in 3.0 wt.% NaCl solution is generally agreed to be adsorption on the metal surface [18,22,23]. This involves the assumption that the corrosion reactions are prevented from occurring over the area (or active sites) of the metal surface covered by adsorbed inhibitor species, whereas these corrosion reactions occur normally over the inhibitor-free area [24]. Figure 3 shows the linear plots for C/θ *versus* C with a correlation coefficient of R^2= 0.9986, suggesting that the adsorption obeys Langmuir's isotherm.

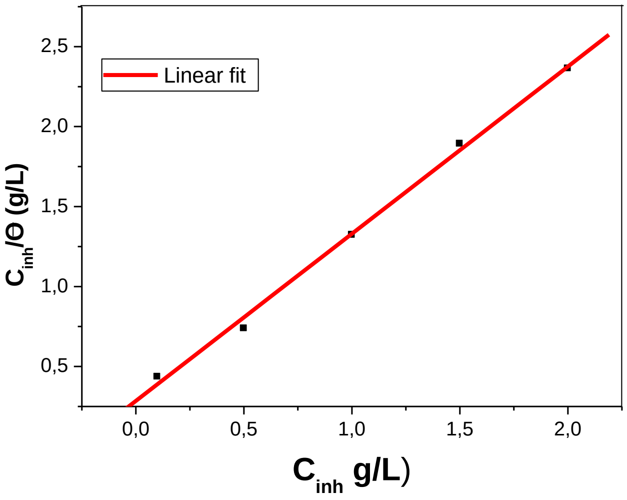

Figure 3. Langmuir adsorption isotherm obtained for CP-Ti in 3.0 wt.% NaCl solution in the presence of different concentrations of inhibitor at 298 K

3.4. Thermodynamic Parameters

The free energy of standard adsorption ΔG_{ads} (kJ/mol) could be estimated from the determined values of K_{ads} as per equation 5:

$$K_{ads} = \left(\frac{1}{55.55}\right) exp\left(\frac{-\Delta G_{ads}}{RT}\right) \tag{5}$$

where, R is the molar gas constant (8.314 J. mol^{-1}.K^{-1}), T is the absolute temperature, and the value of 55.55 is the concentration of water in the solution expressed in M. The calculated values of both K_{ads} and ΔG_{ads} are shown in Table 4.

The thermodynamic activation parameters for the corrosion process of CP-Ti in the absence and presence of different concentrations of EOPL are taken from the Arrhenius-like plot according to Equation 6 in the temperature range of 298.5 to 348.5K [25].

$$LnW = LnA - \frac{E_a}{RT} \qquad (6)$$

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

$$LnW = \left[Ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S_a^0}{R}\right)\right] - \frac{\Delta H_a^0}{RT} \qquad (7)$$

Where N is the Avogadro's number and h is the Planck's constant.

Plots of the logarithm of W, with the reciprocal of absolute temperature (1/T) for CP-Ti in a 3.0 wt.% NaCl solution without and with 0.5 g/L of EOPL are shown in Figure 4.

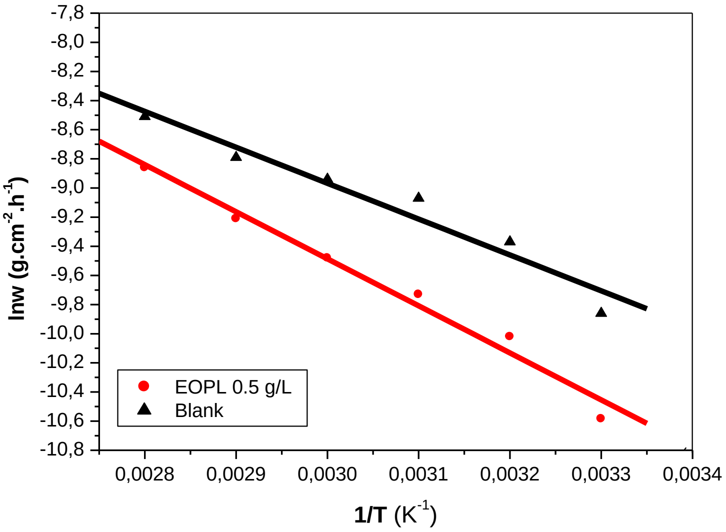

Figure 4. Arrhenius plots for Ti-CP in 3.0 wt.% NaCl solutions containing 0.5 g/L of EOPL

A plot between lnw and (1/T) gives a straight line with a slope of ($\Delta H_a/RT$) and an intercept of [ln(R/Nh) + ($\Delta S_a/R$)] from which the values of enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a) are calculated.

The values in Table 4 specifically show that the value of $\mathbf{E_a}$ in the presence of EOPL is greater than that in the absence of EOPL. Thus, it is clear that the adsorption of EOPL on the surface of CP-Ti blocks the active sites of the saline solution and consequently increases the apparent activation energy because of the development of an adsorbent film by a physical mechanism (electrostatic It can be suggested that the EOPL was absorbed onto the metal surface by a physisorption mechanism [26,27].

The kinetic-thermodynamic parameters cited in Table 4 indicate that the positive values of $\Delta \mathbf{H_a}$ reflect the endothermic nature of metal dissolution process [28]. On comparing the values, $\Delta \mathbf{S_a}$ reveals that $\Delta \mathbf{S_a}$ is more positive in the presence of the inhibitor (EOPL).

The negative value of ΔSa for the solution with inhibitor indicates that the complex activated in the rate-determining step represents an association rather than a dissociation step, indicating that a decrease in disorder takes place during the transition from reactant to activated complex (Figure 5) [29-33].

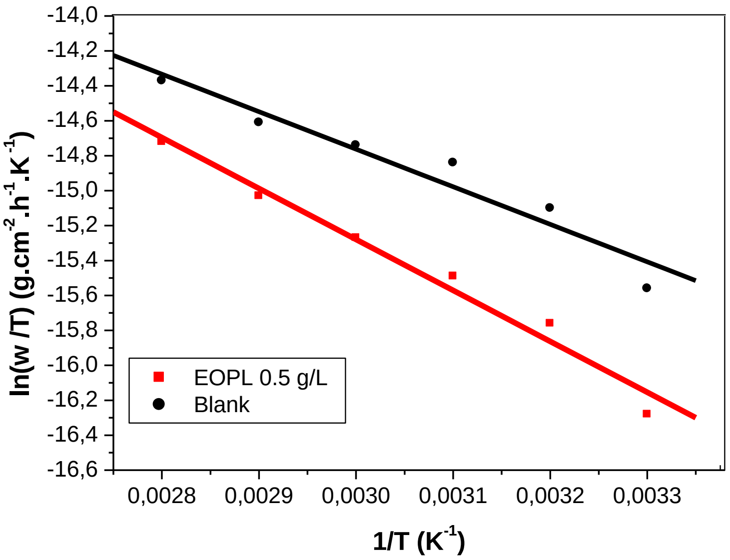

Figure 5. Plots of ln(w/T) vs. 1/T for CP-Ti in 3.0 wt.% NaCl without and with 0.5 g/L of EOPL

Table 4. Thermodynamic and equilibrium adsorption parameters of the inhibitor (EOPL) CP-Ti surface in a 3.0 wt.% NaCl solution

Inhibitor	**E_a** kJ/ mol	**ΔH_a** kJ/ mol	**ΔS_a** J. mol^{-1}.K^{-1}
Blank	21.41	17.86	-173
EOPL	27.97	24.25	-171

3.4. Morphological studies

Figure 6 displays the SEM images of the CP-Ti sample in a solution of 3.0 wt.% NaCl without and with EOPL for 48 hours of immersion (Figure 6 b and 6 c). The SEM images of the surface were badly corroded by the NaCl (Figure 6b). The change in surface roughness (attack by Cl^- ions) explains the formation of oxide on the metal surface, while Figure 6c, displays the sample dipped for the same period of time interval 3.0 wt.% NaCl solution containing 2.0 g/L of EOPL with a lower surface roughness, because of blocking of active site and protecting metal from oxide formation or corrosion [32].

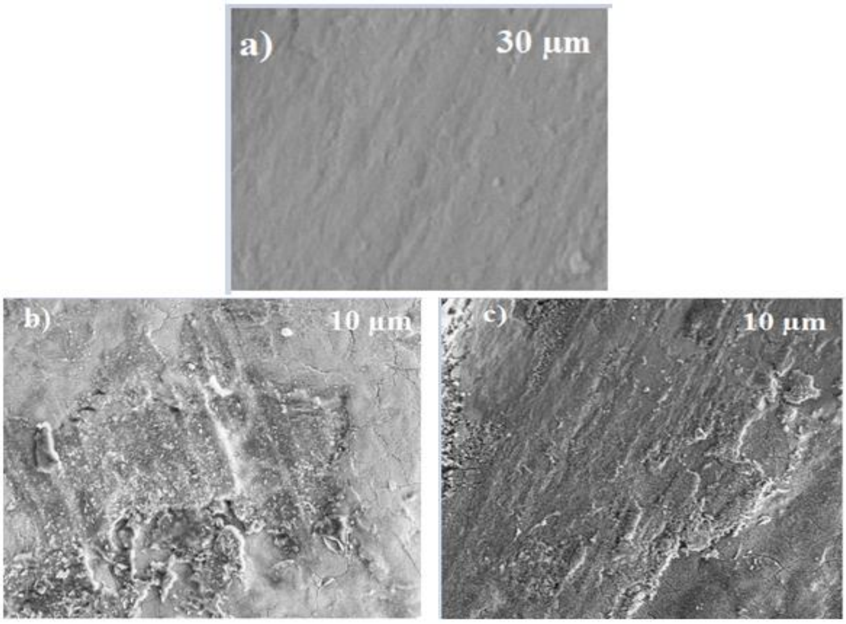

Figure 6. SEM micrographs of the surface of CP-Ti after 48 hours of immersion in 3.0 wt.% NaCl at 298; a) CP-Ti, b) CP-Ti in 3.0 wt.% NaCl without inhibitor, and c) CP-Ti in 3.0 wt.% NaCl containing 2.0 g/L

4. CONCLUSION

The inhibition effect of essential oil of *Pistacia lentiscus* (EOPL) on the corrosion behavior of CP-Ti in a 3.0 wt.% NaCl solution was studied by electrochemical and weight loss methods. The surface morphology was investigated by scanning electron microscopy (SEM).

The result revealed that the efficiency of inhibition increased with increasing inhibitor concentrations. The maximum value obtained was 84.58% at 2.0 g/L.

The potentiodynamic polarization curves showed that the corrosion current decreased from 1.016 to 0.797 µA/cm^2 confirming that a protective film has formed on the metal surface. This controls metal corrosion. The result also showed that the adsorption of *Pistacia lentiscus* oil on the CP-Ti surface in 3.0 wt.% NaCl solution can be described by the Langmuir adsorption isotherm.

The activation energy increases with an increase in inhibitor concentrations, which suggests physisorption. In addition, the enthalpy of activation comes out to be negative, which shows an endothermic process. The SEM micrographs revealed that the addition of the optimal concentration of *Pistacia lentiscus* oil contributed to the protection of the CP-Ti from corrosion. From all the analysis, it could be concluded that the essential oil of *Pistacia lentiscus* (EOPL) acts as an effective, natural and environmentally friendly corrosion inhibitor for commercially pure titanium (CP-Ti) in 3.0 wt.% NaCl medium at 298 K.

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