INHIBITION OF ACID CORROSION OF MILD STEEL BY AQUEOUS EXTRACT OF OLIVE LEAVES

SOUAD TOUAZI

Laboratoire de Valorisation des Energies Fossiles (LAVALEF), Ecole Nationale Polytechnique d'Alger, Algeria

Laboratoire d'Electrochimie, Corrosion et de Valorisation Energétique (LECVE), Faculté de Technologie, Université de Bejaia, Algeria

souad.touazi@yahoo.fr

ADJOUATI BACHIR ABDERAOUF

Laboratoire de Valorisation des Energies Fossiles (LAVALEF), Ecole Nationale Polytechnique d'Alger, Algeria

bachir_abderraouf.adjouati@g.enp.edu.dz

ZIANE AYMENE

Laboratoire de Valorisation des Energies Fossiles (LAVALEF), Ecole Nationale Polytechnique d'Alger, Algeria

aymene.ziane@g.enp.edu.dz

NADIA ZAIDI

Laboratoire d'Electrochimie, Corrosion et de Valorisation Energétique (LECVE), Faculté de Technologie, Université de Bejaia, Algeria

zaidinadia06@gmail.com

MIHAEL BUČKO

University of Defense, Military Academy, Pavla Jurišića Šturma 33, 11000, Belgrade, Serbia

mihaelbucko@yahoo.com

telephone: 011 3603 464

LAID MAKHLOUFI

Laboratoire d'Electrochimie, Corrosion et de Valorisation Energétique (LECVE), Faculté de Technologie, Université de Bejaia, Algeria

laid_mak@yahoo.fr

Abstract: *In this study, a green inhibitor of steel corrosion in acidic solution was prepared from an agricultural waste product based on olive leaves (Olea Europaea Syslvestris). The paper deals with the development of a method for extracting compounds from the plant, their use as corrosion inhibitors in acidic media and their mode of operation. The olive leaves extract, obtained by refluxed technique in water, was tested as a corrosion inhibitor for steel, using different electrochemical methods: open circuit potential monitoring and potentiodynamic (Tafel) curves, as the extract was added in various concentrations into the 0.1 mol dm^{-3} HCl. The results obtained by various techniques showed that the extract acted as a mixed-type inhibitor. Several adsorption isotherms (Langmuir, Temkin and Frumkin) were evaluated to determine the effective adsorption isotherm. It was concluded that the adsorption of the inhibitor was spontaneous, through the mechanism of physical adsorption, and it obeyed the Langmuir adsorption isotherm. The highest corrosion inhibition efficiency of 66 % was obtained for 0.96·10^{-3} g dm^{-3} of inhibitor, as measured by potentiodynamic polarization method.*

Keywords: *corrosion inhibitor, green chemistry, olive leaves, steel.*

1. INTRODUCTION

Corrosion inhibitors are compounds broadly used to prevent or completely inhibit metal corrosion in liquid or gaseous corrosion media. There are plenty of liquid media in military equipment where the application of corrosion inhibitors is mandatory, for example heating/cooling systems, lubrication systems, oils and fuels facilities, hydraulic systems in weaponry, vehicles and radar systems, food processing, equipment decontamination and cleaning, preparation of ordnance for coating application and assembly, etc.

Corrosion inhibitors reduce the metal corrosion rate by various actions, such as adsorption of ions/molecules onto the metal surface, decreasing the diffusion of reactants and products of the corrosion process, or increasing the overpotential for anodic and cathodic reactions of the corrosion process [1].

A vast number of chemicals have been used as inhibitors. The most famous inhibitors in acidic media are nitrogen, oxygen and sulfur-based organic compounds and alkaloids, while in neutral media, chromates, benzoates, phosphates and nitrites are known as excellent corrosion inhibitors [2].

Many research groups have reported the successful use of green inhibitors, i.e. the naturally occurring chemicals that are easily biodegradable. Various natural compounds have been used for this purpose, such as honey, plant juice, oil, seeds and leaves, tree and fruit extracts, etc. [3].

As a continuation of previous efforts in this field, this paper aims to investigate the application of olive (lat. *Olea Europaea Syslvestris*) leaf extract as a corrosion inhibitor for mild steel corrosion in acidic medium. Steel equipment often comes in contact with acidic solutions, in processes like decontamination, acid cleaning, acid descaling, or acid pickling, and all these processes require the presence of corrosion inhibitors. Olive leaves are a cheap raw material, as a by-product in the olive grove farming and olive oil industry in the Mediterranean coastal zone [4].

The role of olive leaves extract in steel corrosion in HCl medium was investigated by the two electrochemical techniques: open circuit potential monitoring and potentiodynamic (Tafel) curves recording.

2. EXPERIMENTAL PART

2.1. Preparation of the corrosion inhibitor and the corrosion medium

The harvest of wild olive leaves was carried out at the National Polytechnic School of Algiers, in the northern Algeria during the flowering period in February 2020. The leaves were washed in distilled water, dried and grounded to obtain the powder. To obtain the extract, a sample of 10 g of olive leaves powder was mixed with 100 ml of distilled water, stirred and heated under reflux at 80° C for 45 minutes. After extraction, the mixture was cooled and separated by filtration using a Büchner funnel and a water pump. The liquid phase was recovered, stored protected from light and subsequently used as a corrosion inhibitor.

The corrosive medium was 100 cm^3 of 0.1 mol dm^{-3} HCl solution at 25 °C, without and with different concentrations of the olive leaf extract.

2.2. Electrochemical techniques

The working electrode in corrosion tests was mild steel, with the chemical composition shown in Table 1. The electrode was polished, degreased with acetone and rinsed in distilled water prior to the immersion in HCl.

Table 1. Chemical composition of steel, wt.%

C	0.15 – 0.26	S	< 0.040
Si	< 0.35	Mo	0.4 – 0.6
Mn	< 1.5	Fe	97 – 98
P	< 0.035		

Open circuit potential (OCP) and potentiodynamic polarization measurements were carried out using a PGZ100 type potentiostat-galvanostat controlled by a Voltamaster software. The reference electrode was K_2SO_4-saturated sulphate electrode (SSE) with an equilibrium potential of 0.655V vs. standard hydrogen electrode at 25 ˚C. Platinum mesh was used as counter electrode in the polarization experiments.

The potentiodynamic plots were obtained at a scan rate of 1 mVs^{-1}, over the respective OCP range between −250 mV and +250 mV, from cathodic to anodic end.

The results of the electrochemical measurements are the mean value of three runs, each with a freshly prepared steel sample and new acid solution. The percentage of inhibition efficiency was calculated using the equation below:

$$IE,\% = \frac{i_{corr} - i_{inh}}{i_{corr}} \qquad (1)$$

where i_{corr} and i_{inh} are the corrosion current densities of steel, in the absence and presence of inhibitor, respectively.

3. RESULTS

3.1. Open circuit potential

Figure 1 depicts the evolution of the open circuit potential of the steel as a function of immersion time in 0.1 mol dm^{-3} HCl, with various concentrations of the aqueous extract of olive leaves. The curves obtained were compared with a reference curve obtained without the inhibitor.
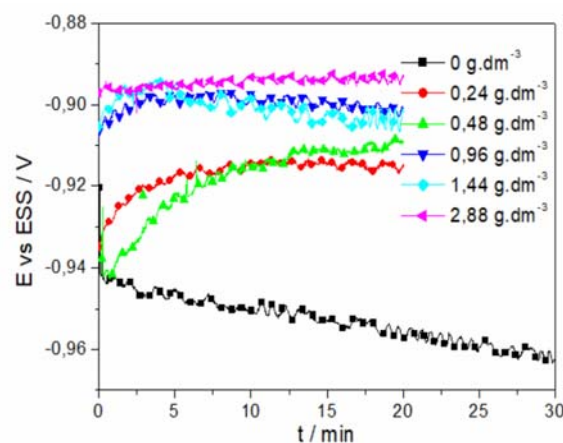

Figure 1. Monitoring of the open circuit potential of mild steel immersed in 0.1 mol dm^{-3} HCl at different concentrations of olive leaf extract

In the absence of the extract of olive leaves, it is noted that the evolution of the potential of steel tends towards more negative values, indicating the degradation of the metal. The stabilization of the OCP at a value of -0.96 V is achieved after 25 minutes of immersion. On the other hand, when the tests are conducted in the presence of the green inhibitor, a displacement of the potential towards more positive values is observed. This ennoblement of the potential indicates that there is a formation of a protective

layer on the metal surface, which can be attributed to the adsorption of the inhibitor on the active sites of the metal [4, 5].

It should be noted that the potential stabilization time decreases as the concentration of the extract increases, up to an added value higher than or equal to 0.96 g dm^{-3}. For these values of the inhibitor concentration, the value of the free potential stabilizes already in the first minutes of immersion.

3.2. Polarization curves

The potentiodynamic plots presented in Fig. 2, for various concentrations of the inhibitor added, show similar shape on both anodic and cathodic part, however the values of the corrosion potential and corrosion current density differ significantly.
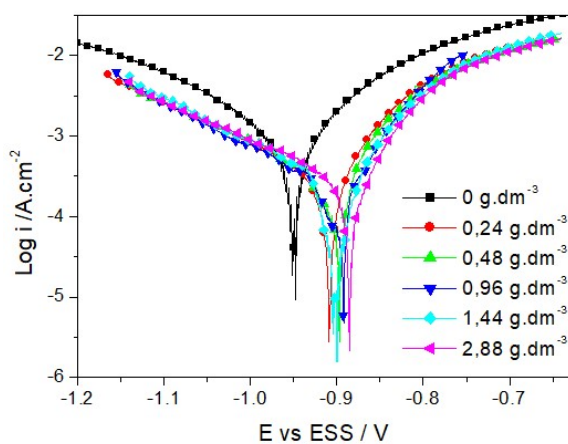

Figure 2. Cathodic and anodic polarization curves of steel in 0.1 mol dm^{-3} HCl with different inhibitor concentrations of olive leaf extract; potential sweep rate is 1 mV s^{-1}

The electrochemical parameters deduced from the potentiodynamic polarization curves, namely: corrosion current density (i_{corr}), corrosion potential (E_{corr}), cathodic and anodic slopes (βc and βa), polarization resistance (Rp) and the inhibition efficiency (IE), are grouped in Table 2. It may be deduced from the data that the increase in the concentration of the extract shifts the corrosion potential towards positive values, decreases the current densities of the anodic and cathodic branches.

Table 2. Electrochemical parameters of steel corrosion in HCl, extracted from the polarization curves

c, g dm^{-3}	E_{corr}, mV	i_{corr}, mA cm^{-2}	βa, V dec^{-1}	βc, V dec^{-1}	IE, %
0	-950	0.48	89	-110.3	-
0.24	-908	0.26	85.5	-179.1	45.9
0.48	-901	0.18	64.6	-140.6	61.4
0.96	-896	0.16	66.2	-141.1	65.9
1.44	-899	0.18	74.3	-134	61.8
2.88	-885	0.24	80	-189.5	50.4

The observation of the polarization plots shows that independently on the inhibitor concentration, the difference in corrosion potential (in the absence and in the presence of the inhibitor) is less than 85 mV and that the

two partial currents (anodic and cathodic) are almost equally reduced. These observations point to the mixed nature of the inhibitor [6] and clearly show that the olive leaf extract reduces both the rate of anodic dissolution of steel described by the reaction (Eq. 2)

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (2)$$

and cathodic reduction of hydrogen protons (Eq. 3)

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (3)$$

In view of the results obtained, one can also notice that the addition of the extract does not modify the shape of the anodic and cathodic branches, which reflects in an insignificant variation in the values of the Tafel coefficients (βa and βc). This result suggests that the adsorbed inhibitor acts by simple blocking of the cathodic and anodic sites. In other words, the inhibitor decreases the surface of the interface between the metal and the electrolyte, without affecting the corrosion mechanism [7].

The results obtained in Table 2 show clearly that the inhibition efficiency was improved with the increase in the concentration of the extract and reached a maximum value of 65.9% for an optimal concentration of 0.96 g.dm^{-3}. Beyond this concentration a decrease of the value of the inhibition efficiency is observed.

3.3. Adsorption isotherms and the inhibition mechanism

Several adsorption isotherms (Langmuir, Temkin and Frumkin) were evaluated to determine the effective isotherm that best describes the adsorption of olive leaves extract on the steel surface in HCl solution. The isotherms are described by the following equations [8]:

Langmuir:

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

Temkin:

$$\exp(-2a\theta) = KC \qquad (5)$$

Frumkin:

$$\frac{\theta}{1-\theta}\exp(-2a\theta) = KC \qquad (6)$$

where θ is the cover degree of the metal surface by the adsorbed inhibitor, defined by the following relationship

$$\theta = \frac{i_{corr} - i_{inh}}{i_{corr}} \qquad (7)$$

where i_{corr} and i_{inh} are the corrosion current densities of steel, in the absence and presence of inhibitor, respectively.

The Figures 3, 4, 5 illustrate the three adsorption isotherms, while Table 3 shows the correlation coefficient obtained by the three different models:

Table 3. Coefficient of correlation, R^2, between the data predicted by the adsorption model and the measured data

for the adsorption process of olive leaves extract on steel

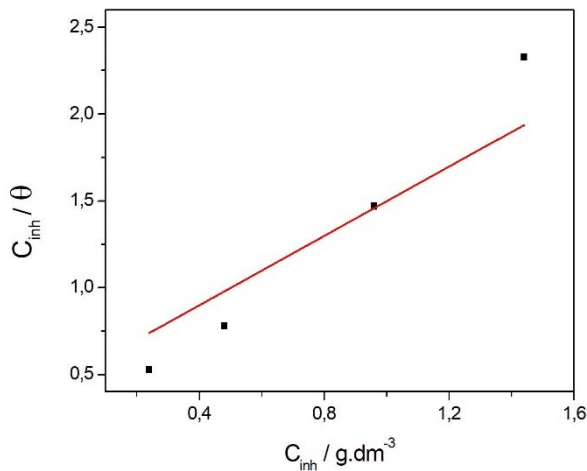| Model	R^2
Langmuir	0.981
Temkin	0.680
Frumkin	0.299

Figure 3. Langmuir adsorption isotherm of olive leaf extract on steel in 0.1 mol dm^{-3} HCl
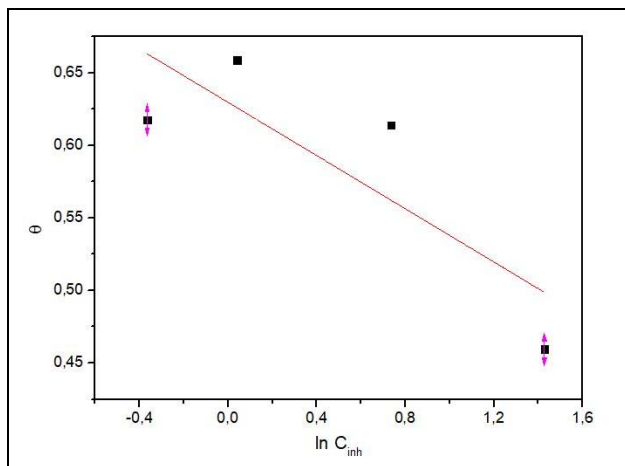

Figure 4. Temkin adsorption isotherm of olive leaf extract on steel in 0.1 mol dm^{-3} HCl
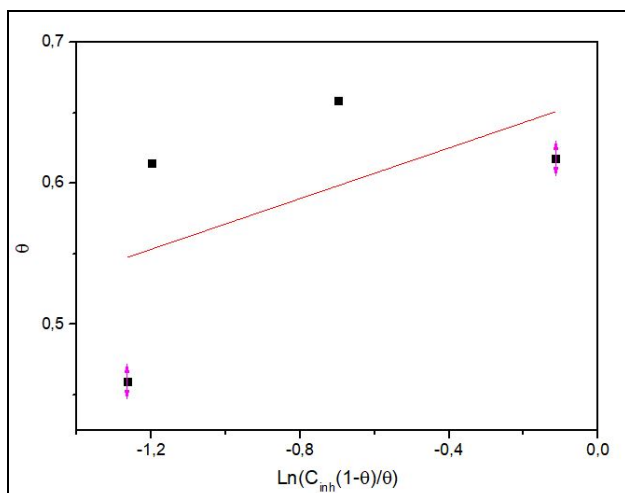

Figure 5. Frumkin adsorption isotherm of olive leaf extract on steel in 0.1 mol dm^{-3} HCl

Analysis of different figures, allows us to note that the only curve that shows linear behavior is the plot of (C_{inh}/θ) as a function of the concentration of inhibitor (Figure 3), presenting the highest correlation coefficient (Table 3). This leads to the conclusion that the adsorption of the olive leaf extract on the surface of mild steel in hydrochloric acid medium obeys the Langmuir adsorption isotherm. Thus, the equilibrium constant (K) can be calculated from the ordinate at the origin of the linear curve C/θ which gives the value (1/K). The parameter K is related to the free energy of adsorption (ΔG), the enthalpy of adsorption (ΔH) and the standard entropy of adsorption (ΔS)° according to the equations (8 – 10):

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G_{ads}^{\circ}}{RT}\right) \quad (8)$$

$$K = \exp\left(-\Delta H_{ads}^{\circ}/RT\right) \quad (9)$$

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (10)$$

The values that describe the adsorption process for the organic molecules of the inhibitor are presented in Table 4:

Table 4. Thermodynamic parameters of the inhibitor adsorption on mild steel

Parameter	Value
ΔS° (J mol^{-1}°K^{-1})	33.39
ΔH° (kJ mol^{-1})	-1.76
ΔG° (kJ mol^{-1})	-11.71

The negative value of the adsorption free energy indicates that the adsorption process is spontaneous. The value of the equilibrium constant K (K = 2.04 dm^3 kg^{-1}) is very low which indicates that the adsorption of the inhibitor on the steel surface is not strong. This result is in correlation with the result obtained during the kinetic study where the inhibition efficiency was not close to 1. Several researchers [6, 8] proposed that the values of the free energy of adsorption close to –20 kJ mol^{-1}, correspond to the electrostatic interactions between the charged molecules and the charges of the metal surface (physisorption), while on the other hand, when the free energy of adsorption is close to –40 kJ mol^{-1}, it corresponds to the transfer of charges between the molecules of the inhibitor and the surface of the metal and thus forming covalent bonds (chemisorption). In our case, the calculated values of the free energy of adsorption indicate that the process is characterized as a physisorption.

The negative values obtained for the enthalpy of adsorption show that the system studied is exothermic. As one can notice, there is an increase in the molecular disorder (ΔS°) with the adsorption of the inhibitor. We can therefore conclude that the phenomenon of adsorption disturbs the order of atoms on the surface of mild steel.

4. CONCLUSION

The scope of this work was to investigate whether the olive leaves extract may be applied as an inhibitor of mild steel corrosion in 0.1 mol dm^{-3} HCl solution. The open circuit potential monitoring and the potentiodynamic curves analysis clearly show that the steel corrosion rate

decreases as the extract is added to the solution in higher concentration. The extract acts as a mixed type inhibitor, since it retards both the anodic and cathodic process of corrosion. Based on the analysis of the adsorption isotherms, it may be concluded that the adsorption of the inhibitor is quite weak, as a result of the physisorption. The future research is going to be focused on the identification of active components in the olive leaves powder that are responsible for the observed inhibitive behavior of the extract.

Acknowledgment

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