Olea europaea Subsp. *Cuspidata* Wood Tar Oil as Anticorrosion for Mild steel in Acidic Media

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Corrosion is one of the serious problems in industry, specially acidic corrosion which is caused by acidic solutions which are widely used in acid cleaning, acid pickling and acid descaling. Mild steel (MS) is widely used in the the industrial field is vulnerable to be corroded by the acidic solution. In the industrial media, corrosion processes are responsible for the loss of metals. There are various methods to mitigation the degradation or destruction of metal surface. Using inhibitors is one of the most potent methods in control of corrosion is due to its low cost and eases of application and practice. As the concern is focused on the safety of any industrial process in health and environment, the use of organic plants as corrosion inhibitors is in the forefront in the current trend of corrosion inhibition studies. In the last decades the need of novel corrosion inhibitor compounds has become more and more stringent. In this study, the efficiency of the bark of *Olea europaea* subsp. *Cuspidata* as corrosion inhibitor for mild steel in 1.0 M sulphuric acid was studied by electrochemical measurements [potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS)]. The results showed that *Olea europaea* subsp. *Cuspidate* wood tar oil acts as a potent corrosion inhibitor and the performance of the inhibitor varied with concentrations for mild steel in 1.0 M H_2SO_4 + 10 % EtOH. The maximum inhibition (%) was 94.97 %, the results were supported by different techniques used. Electrochemical analysis indicated that *Olea europaea* subsp. *Cuspidata* wood oil tar extract acts as mixed mainly cathodic inhibitor. Also, surface analysis the scanning electron microscope (SEM) was carried out to determine the corrosion inhibition property of *Olea europaea* subsp. *Cuspidata* wood tar oil in (1.0 M H_2SO_4 + 10 % EtOH) solution. The adsorption of the wood tar extract on mild steel surface followed Langmuir isotherm.

Keywords: Mild steel, Corrosion, *Olea europaea* subsp. *Cuspidate* wood tar oil, Electrochemical techniques, Adsorption.

INTRODUCTION

In the last few decades, corrosion inhibition is getting more attention economically and environmentally. Corrosion inhibition is favoured to prevent metal dissolution and acid consumption; which is due to its low cost and simplicity of application [1-3]. As the interest in using of environmentally safe materials and products increases, many researches were focused on developing low-cost and eco-friendly corrosion inhibitors. These natural organic inhibitors could be either synthesized or extracted from aromatic herb species or medicinal plants [2]. Several studies have discussed the use of such extract to mitigate the corrosion of metals either in acidic or alkaline environment. Plants are not only safe, eco-friendly and biodegradable in

nature but also, it is viewed as a rich source of naturally occurring chemical organic compounds could be used in many applications and also could be extracted by methods with low cost and simple manner. Leaves, seeds and peels extract of many plants were studied extensively and many of them proved to possess corrosion inhibition activity [4-18].

Corrosion inhibition activity of leaves of rosemary plant was studied for aluminum alloy in sodium chloride environment [19]. El-Etre investigated *Opuntia* extract as green corrosion inhibitor for aluminum metal [20]. Yee [21] determined the inhibitive effect of *Rosmarinus officinalis* L and honey on four metals: aluminum, copper, zinc and iron, in sodium chloride and sodium sulfate solutions. Recently, some researchers studied the use of drugs as corrosion inhibitors

[22,23]. The inhibition of the corrosion of aluminum in hydrochloric acid solutions was studied using extracts of *Delonix regia* [24]. Okafor *et al.* [25] studied natural honey as corrosion inhibitor for metals and alloys of C-steel in high sea water. Umoren *et al.* [26], used gum arabic (GA) and polyethylene glycol (PEG) as corrosion inhibitors for mild steel in H_2SO_4. It was found that PEG was more effective than gum arabic. Odiongenyi *et al.* [27] reported that the ethanolic extract of *Vernonia amygdalina* works as a good inhibitor for the corrosion of mild steel in H_2SO_4 and it obey Langmuir adsorption isotherm. Quariachi *et al.* [28] also reported the inhibitory effect of *Rosmarinus officinalis* oil as green inhibitors on C38 steel corrosion in 0.5 M H_2SO_4. Eddy *et al.* [29] studied inhibition corrosion of mild steel by ethanolic extract of Musa peel by hydrogen evolution and thermometric methods. Rani and Selvaraj [30] reported the inhibition efficacy of *Punica granatum* extract on the corrosion of Brass in 1.0 M HCl using mass loss measurements at different temperatures and various immersion time. A patent was recorded by Turkustani *et al.* [31] for the effect of *Olea europaea* subsp. *Cuspidata* wood tar oil as metals anticorrosion.

It is well known that the main use of heavy wood tar oil was in preserving wooden vessels and objects against rot, as it is waterproof agent. Mid and light wood tar oils also used as wood protection, shining and glossing agents. A dilution of tar oil called "tar water" has numerous uses: *e.g.* a flavouring for candies and alcohol, a spice for food, and scent steam for saunas, as an antidandruff agent in shampoo, and a component of cosmetics.

The olive tree, *Olea europaea*, one of the perennial plants which has been cultivated for olive oil, fine wood, olive leaf and the olive fruit. The olive tree is very hardy, drought-resistant, disease and fire-resistant. Its root system is robust and capable of regenerating the tree even if the above-ground structure is destroyed.

Virgin olive oil contains glycerides, hydrocarbons, tochopherols, linear short/long chain alcohols and their esters, sterols and their esters, α-methyl sterols, triterpenic acids, phytol, geranylgeraniol, monohydroxy triterpenes, dihydroxy triterpenes, phenols, flavour components, methyl and ethyl esters.

The present study, based on the fact that the corrosiveness caused by aqueous media, including acids or alkaline on metals can be reduced by adding an inhibitor to such media. Moreover, we must continually confronted with metals corrosion problem, which endangers safety; environment and economic motives. Due to these problems and to the indiscriminate uses of artificial inhibitors, which hinder metal corrosion and because of their side effects, on the environment, including aqueous media, effective natural alternatives with desirable side effects, therefore needed. There were some previous studies on plant extracts, which may have anticorrosion properties. However, as far as we know no practical anticorrosion studies conducted on Wood tar oil of *Olea europaea* subsp. *Cuspidata,* especially those growing in Saudi Arabia (Albaha district).

The present work provides a new approach in using plant wood tar oil of *Olea europaea* subsp. *Cuspidata* produced by the wood destructive distillation as mild steel anticorrosion in acidic solution (1 M H_2SO_4 + 10 % EtOH).

EXPERIMENTAL

A stock solution of corrosion media in sulfuric acid (98 %) was prepared from analytical reagent grade using bi-distilled water. For electrochemical measurements, the experiments were carried out in solution of 1.0 M H_2SO_4 + 10 % EtOH.

Mild steel sample in the form of disc shape and of composition (wt. %) (Table-1) was used for the corrosion tests. Specimen was polished with different grades of emery paper from 100 up to 1200. It suspended in solution inside the test cell filled with acid and the added corrosion inhibitor, the test cell placed in a water bath at 30 ± 0.1 °C. After 1 h the potentiodynamic polarization (PDP) and electrochemical impedance (EIS) measurements, taken and recorded.

TABLE-1
MILD STEEL SAMPLE COMPOSITION

Element	Wt %	Element	Wt %
Carbon	≤ 0.20	Phosphorous	≤ 0.01
Silicon	≤ 0.02	Chromium	≤ 0.06
Manganese	≤ 0.10	Aluminum	≤ 0.03
Nickel	≤ 0.04	Iron	≥ 99.54

Olea europaea subsp. *Cuspidata* wood tar oil (Viscosity = 1.8689 millipoise) was extracted using the destruction distillation, during May, 2014 from Albahah district (19°59'14.12"N, 41°27'53.01"E) southwest Saudi Arabia from cool summit at 2242 M.A.S.L. Species status of this plant was fervid at Faculty of Sciences Herbarium (Serial No. 1597), King Abdul-Aziz University, Jeddah.

Electrochemical measurements: Electrochemical measurements achieved by connecting the cell with a capacity of 250 mL to ACM Gill AC instrument and to a Samsung computer (Bridge DVD ASUS 8X max). A platinum electrode as counter electrode and Ag/Ag_2Cl_2/Cl⁻ electrode as reference electrode were used. The working electrode (WE) was in the form of a disc and with an exposed area of 0.0362 cm².

All experiments were carried out in (1.0 M H_2SO_4 + 10 % EtOH) solutions at 30 ± 0.1 °C using a thermostat. To proved sufficient for E_{ss} (the steady-state potential), stabilization period of 1 h was found prior to the impedance measurement.

Tafel polarization curves were recorded by automatically changing the potential from -700 to -200 mV with scanning rate of 0.5 mV s⁻¹. The polarization resistance measurements performed by applying a controlled potential scan over a small range typically 20 mV with respect to E_{corr}. Slope of the resulting current linearly plotted against potential at E_{corr}, being the polarization resistance (R_p). Nyquist plots were obtained from impedance measurements and were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz – 100 mHz, with a signal amplitude perturbation of 10 mV. The inhibition efficiency (Inh. %) has been calculated from PDP by the measured I_{corr} values using the equation:

$$Inh_{I_{corr.}}\ (\%) = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right) \times 100 \tag{1}$$

where the corrosion current density in the absence and presence of inhibitor are i^o_{corr} and i_{corr}, respectively.

And Inh. % has been obtained from R_{ct} values using the relationship:

$$\text{Inh}_{R_{ct.}} \ (\%) = \left(1 - \frac{R_{ct}^{o}}{R_{ct}}\right) \times 100 \qquad (2)$$

where the charge transfer resistance in the absence and in presence of inhibitor are R_{ct}^{o} and R_{ct}, respectively.

Scanning electron microscopy (SEM): After the corrosion experiments, SEM studies was taken for the samples to know the surface condition before and after corrosion in the absence and presence of inhibitor. The scanning electron microscope images of the samples were recorded using Digi scope II V2.

Morphology of the samples was studied after accomplishing the corrosion experiments using the scanning electron microscope to investigate the surface morphology change before and after corrosion in the absence and presence of inhibitor. The scanning electron microscope images of the samples were recorded using Digi scope II V2.

RESULTS AND DISCUSSION

Potentiodynamic polarization (PDP) measurements: Measurements of potentiodynamic polarization curves were carried out at 30 ± 0.1 °C in 1.0 M H_2SO_4 + 10 % EtOH with various concentrations of the bark of *Olea europaea* subsp. *Cuspidata* wood tar oil extract to study the kinetics of the cathodic and anodic reactions. Fig. 1 illustrates polarization behaviour of mild steel in 1.0 M H_2SO_4 in the absence and presence of different concentrations of wood tar extract after 1 h. of immersion. It is obvious from Fig. 1 that both the anodic branch and the cathodic branch of the polarization curve are affected, but the cathodic reaction is more influenced by the inhibitor, indicating that the wood tar extract acts as mixed type mainly cathodic inhibitor. This result shows that the addition the bark of *Olea europaea* subsp. *Cuspidata* wood tar extract retards both the dissolution and the hydrogen evolution reactions. It is also clear that the inhibition efficiency increases as the increase in inhibitor concentration, but the cathodic reaction is more inhibited, meaning that the addition of wood tar extract reduces (alter) the dissolution of mild steel (anodic reaction), also hinder the hydrogen evolution (cathodic reaction). Therefore, the investigated *Olea europaea* subsp. *Cuspidata* wood tar extract can be classified as mixed type mainly cathodic inhibitor.
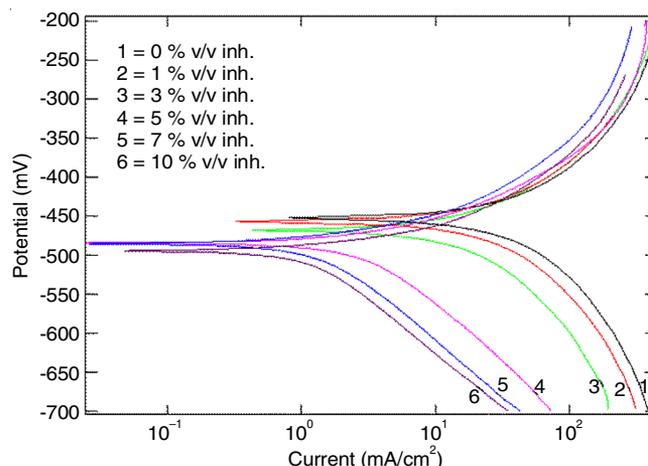

Fig. 1.   Potentiodynamic polarization curves for mild steel in 1.0 M H_2SO_4 containing different concentrations of *Olea europaea subsp. Cuspidata* wood tar oil at 30 °C

Table-2 gives the values of kinetic parameters such as corrosion potential (E_{corr}), corrosion current densities (I_{corr}), the anodic Tafel slope (b_a), cathodic Tafel slope (b_c) and inhibition efficiency (Inh. %) were calculated from the curves of Fig. 1.

The rate of corrosion current densities (I_{corr}) decreases with increasing concentration of wood tar, maximum value of inhibition efficiency 94.97 % achieved at 10 %v/v. It can obvious that the inhibition efficiency increases with increasing wood tar concentration.

From Table-2, it is concluded that:

• E_{corr} shifted to more negative values (less negative) in irregular way upon addition of the wood tar extract. The changed indicating that this behaviour reflects the wood tar extract ability to inhibit the corrosion of mild steel in 1.0 M H_2SO_4.

• The I_{corr} values was decrease with increasing wood tar concentration.

• The cathodic Tafel slopes (b_c) vary over a range of 180-108 mV/dec for wood tar extract. Therefore, the cathodic and anodic slopes values change with increasing concentration of *Olea europaea* subsp. *Cuspidata* wood tar oil in 1.0 M H_2SO_4. This result indicates the influence of the wood tar (inhibitor) on the kinetics of the hydrogen evolution reaction and dissolution reaction [32,33].

• The values of Inh. (%) increase with increasing the inhibitor (wood tar) concentration reaching a maximum value (94.97 %) at 10 % v/v.

TABLE-2
ELECTROCHEMICAL PARAMETERS AND INHIBITION EFFICIENCIES FROM IMPEDANCE & POLARIZATION MEASUREMENTS FOR THE CORROSION OF MILD STEEL IN THE ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF *Olea europaea* subsp. *Cuspidata* WOOD TAR OIL AT 30 °C

Conc. (% v/v)	Polarization				Impedance			Inhibition (%)	
	$-E_{corr.}$ (mV)	$I_{corr.}$ (mA)	b_a (V/dec)	b_c (V/dec)	$R_{sol.}$ (ohm cm^2)	R_{ct} (ohm cm^2)	$C_{dl} \times 10^3$ (μF cm^{-2})	Inh.$_{Icorr.}$ (%)	Inh.$_{Rct.}$ (%)
0.0	454.98	50.119	148.63	180.50	0.3918	1.404	3.119	–	–
1.0	470.22	21.965	83.89	139.12	0.4267	3.233	2.296	56.17	56.57
3.0	484.45	18.438	62.54	132.65	0.4322	4.766	1.091	63.21	70.54
5.0	486.49	12.674	56.63	132.54	0.4409	6.766	0.9205	74.71	83.68
7.0	490.62	7.7080	55.11	140.01	0.4451	9.648	0.3705	84.62	85.44
10.0	491.57	2.5190	49.49	108.15	0.4915	27.26	0.1204	94.97	94.85

• The *Olea europaea* subsp. *Cuspidata* wood tar oil is a mixed type mainly cathodic inhibitor with small shift in anodic values.

Electrochemical impedance spectroscopy (EIS) measurements: EIS is a powerful measurement in the corrosion study. Electrode kinetics, surface properties and information of the mechanism can be obtained from impedance diagrams [34-38]. Nyquist plots obtained in the absence and the presence of different concentrations of studied *Olea europaea* subsp. *Cuspidata* wood tar oil for mild steel in 1.0 M H_2SO_4 + 10 % EtOH solution at 30 ± 0.1 °C are presented in Fig. 2. The curves show a similar type of Nyquist plots in the presence of various concentrations of wood tar extract. The size of the capacitive loop increases with the addition of wood tar extract, shows that a barrier gradually forms on the surface of mild steel. The Nyquist plots do not yield perfect semicircles and give deviation from ideal semicircle as expected from the theory of EIS. The deviation from ideal semicircle was attributed to the frequency dispersion as well as to the inhomogeneities of the sample surface [38].
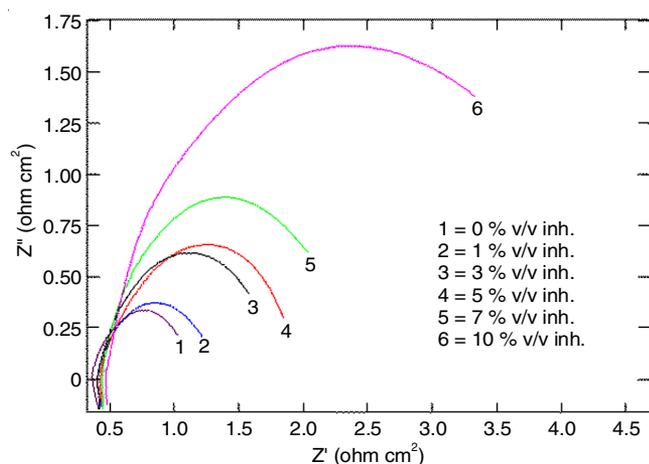

Fig. 2.   Nyquist plots for mild steel in 1.0 M H_2SO_4 solution in the absence and in the presence of different concentrations of *Olea europaea* subsp. *Cuspidata* wood tar oil at 30 °C

In corrosion study electrochemical impedance spectroscopy (EIS) is one of the main measurements. From impedance diagrams electrode kinetics, surface properties and information of the mechanism could be obtained [34-38]. Nyquist plots obtained in the absence and the presence of different concentrations of studied *Olea europaea* subsp. *Cuspidata* wood tar oil for mild steel in 1.0 M H_2SO_4 + 10 % EtOH solution at 30 ± 0.1 °C are presented in Fig. 2. The curves show a similar type of Nyquist plots in the presence of various concentrations of wood tar extract. The size of the capacitive loop increases with the addition of wood tar extract shows that a barrier gradually formed on the surface of mild steel. The Nyquist plots do not yield perfect semicircles and give deviation from ideal semicircle as expected from the theory of EIS. The deviation from ideal semicircle was attributed to the frequency dispersion as well as to the inhomogeneity of the sample surface [38].

Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values obtained from Nyquist plots are recorded in Table-2. Maximum value of inhibition efficiency (Inh. %) for the extract (94.85 %) was achieved at 10 % v/v.

By analyzing Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircle, meaning that the process of corrosion was controlled by charge-transfer [39-41]. Generally, the shape of the Nyquist curves is very similar for all samples and solutions (in the absence or the presence of inhibitors) indicating that no changes in the corrosion mechanism [42]. From the EIS data (Table-2), it is concluded that the value of R_{ct} increases from 1.404 ohm cm^2 to 27.26 ohm cm^2 with increasing the concentration of the wood tar extract and this indicates an increase in Inh. %, which in agreement with the results obtained from polarization. In fact, the presence of inhibitors enhances the value of R_{ct} in acidic solution. Values of C_{dl} are also brought down to the maximum extent in the presence of wood tar inhibitor and the decrease in the values of C_{dl} follows the order similar to that obtained for I_{corr} in PDP study. The decrease in C_{dl} from 3.119×10^{-3} to 0.1204×10^{-3} μF cm^{-2} results from an increase in the thickness of the double layer and/or a decrease in dielectric constant, suggesting that *Olea europaea* subsp. *Cuspidata* wood tar extract inhibit the mild steel corrosion *via* adsorption at metal/acid interface [43,44]. The advantages of EIS measurement are to follow the corrosion behaviour of the metal with constant time.

The EIS of the inhibitor were analyzed using the equivalent circuit (Fig. 3) which fits well with our experimental results and represents a single charge transfer reaction. In the analysis, simple Randel's electrical equivalent circuit with one time constant was used in which the ideal capacitor was replaced by a constant phase element. In the diagram, R_s represents the solution resistance; C_{dl} in the circuit represents the capacitance of electrical double layer on the metal surface; R_{ct} stands for the charge transfer resistance. There is relatively good agreement between the polarization resistances, obtained from both electrochemical methods.
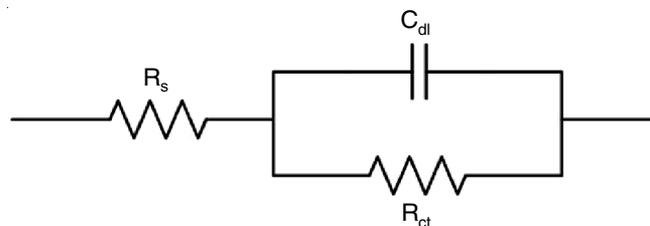

Fig. 3. Electrical equivalent circuit used for fitting EIS data

Scanning electron microscopy (SEM): SEM micrographs of the mild steel surface was taken to establish the changes that occur throughout the corrosion of mild steel in the absence and presence of the wood tar extract. Fig. 4(a) illustrates that the image of mild steel surface immersed in 1.0 M H_2SO_4 is highly corroded, it could be concluded that the surface of mild steel sample is damaged in aggressive acid 1.0 M H_2SO_4. Fig. 4(b) illustrates a surface with adsorbed inhibitor on the mild steel surface after the addition 10 % v/v of wood tar extract to 1.0 M H_2SO_4. It is obvious from SEM images that the irregularities in the mild steel surface due to corrosion is absent in the inhibited surface and the surface is almost free from corrosion.

Inhibition efficiency: The reduced in the corrosion rate by the addition of wood tar extract of *Olea europaea* subsp. *Cuspidata* is attributed to rather adsorption of the compounds
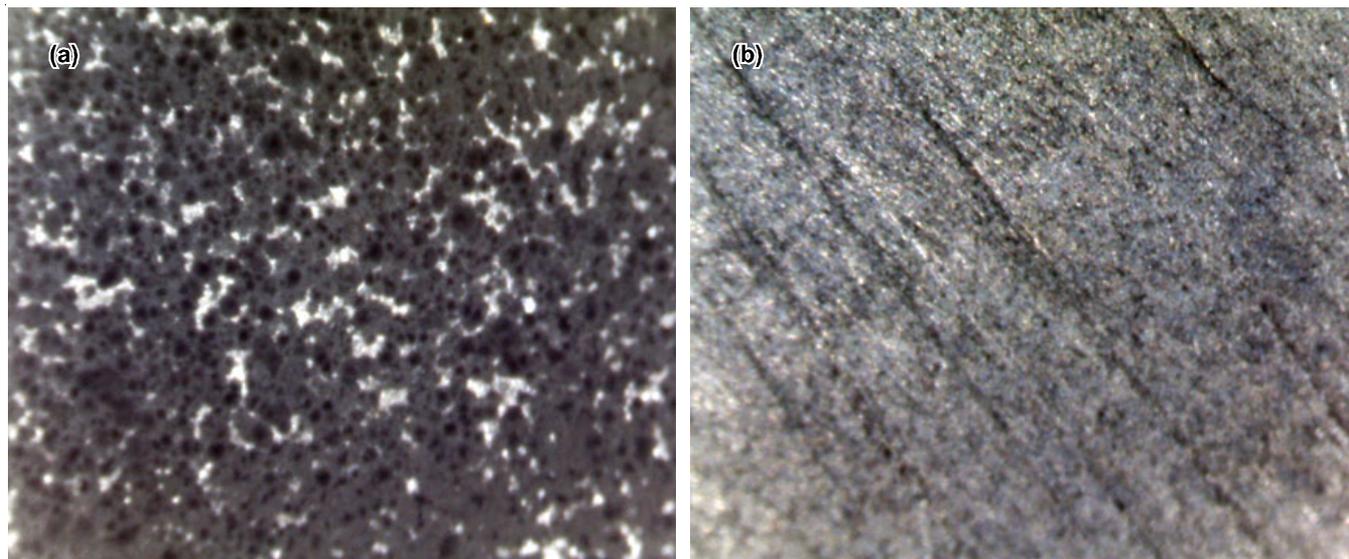
Fig. 4. SEM images of the surface of mild steel after immersion for 1 h in 1.0 M H_2SO_4 solution at 30° C (a) in the absence of *Olea europaea* subsp. *Cuspidata* wood tar oil, (b) in the presence of 10 % v/v of *Olea europaea* subsp. *Cuspidata* wood tar oil

occur in the extract on the metal surface or the formation of the barrier film separating between the metal surface and the corrosive medium [45-47]. *Olea europaea* subsp. *Cuspidata* wood tar extract compounds contain the functional groups in its skeleton, the corrosion inhibition by this oil in H_2SO_4 solution, most probably *via* adsorption by the π electron on the functional groups.

Fig. 5 shows the variation of inhibition efficiency (Inh. %) with concentration of the investigated extract (% v/v) from PDP and EIS measurements, the figure shows a good agreement between the PDP and EIS data. As it could be readily seen from the figure, the plots have the form of S- shaped adsorption isotherm. This indicates that this extract of *Olea europaea* subsp. *Cuspidata* wood tar oil inhibit the dissolution of mild steel in the acid by adsorption at the mild steel/acid solution interface.
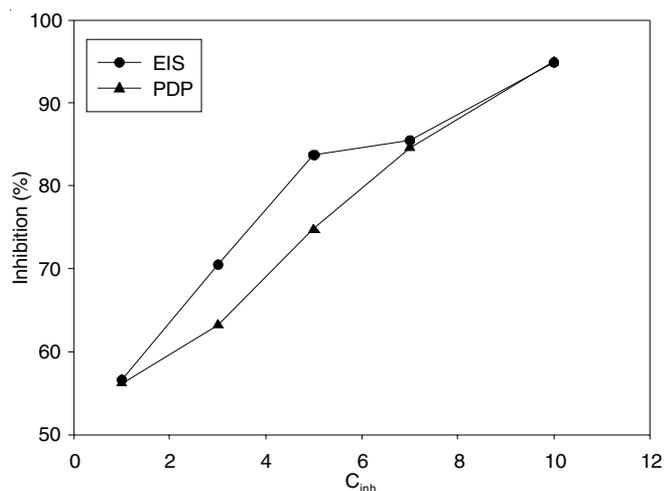

Fig. 5. Relation between concentration of inhibitor *vs.* inhibition efficiency at 30 °C

Inhibition mechanism: The study of inhibition mechanism requires elaborated knowledge of the essential interaction between the protective compound and the metal surface. The polar unit present in the inhibitor is considered as the center of the reaction for the chemisorption process. Furthermore; the orientation, shape, size and electric charge on the inhibitor molecule determine the degree of adsorption and the activity of inhibitor. Increase in inhibition efficiencies with the increase of concentration of *Olea europaea* subsp. *Cuspidata* wood oil tar illustrates that the inhibition effectiveness is due to adsorption of inhibitor molecules on the surface of mild steel sample. Generally, the mechanism of corrosion inhibition in acid solution is by the adsorption of inhibitor molecule onto the metal surface by one of the four types of adsorption:
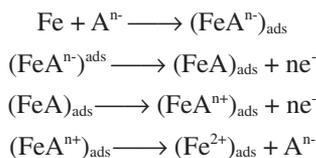
• Attraction by electrostatic force between the charged molecules and charged metal.

• The interaction between unshared electron pairs in the molecule and the metal.

• Interaction of π-electrons with the metal surface.

• All of the above [48-50].

As illustrate from PDP and EIS measurements, corrosion of mild steel in 1 M H_2SO_4 is retarded (hindered) in the presence of different concentrations of *Olea europaea* subsp. *Cuspidata* wood oil tar. The results clearly showed that the inhibition efficiency increases with increasing the wood tar extract concentration, which suggested to form an insoluble complex adsorbed on mild steel surface *via* adsorption process, leading to more inhibition efficiency, this insoluble complex may leads to blocking most of the active centers on mild steel sample surface and therefore, increasing the surface coverage which indicates a steady inhibition is found.

In acidic media, the molecule of inhibitor exists as protonated shape. These protonated species adsorb on the cathodic sites of mild steel sample and hinder the evolution of hydrogen. The interactions between π electrons of heterocyclic compounds and the lone pair of electrons on nitrogen and oxygen atoms found in *Olea europaea* subsp. *Cuspidata* wood oil tar inhibitor (donor acceptor interactions) was occurred which the adsorption on anodic region can occur directly lead to decrease the anodic dissolution of mild steel sample [51].

There are two reactions occur, anodic and cathodic reactions. The corrosion mechanism of iron and its alloys in acidic medium are proposed as follows [52-55]:

Anodic reaction (oxidation reaction):

$$Fe + A^{n-} \longrightarrow (FeA^{n-})_{ads}$$

$$(FeA^{n-})^{ads} \longrightarrow (FeA)_{ads} + ne^-$$

$$(FeA)_{ads} \longrightarrow (FeA^{n+})_{ads} + ne^-$$

$$(FeA^{n+})_{ads} \longrightarrow (Fe^{2+})_{ads} + A^{n-}$$

Cathodic (reduction reaction or hydrogen evolution reaction):

$$Fe + H^+ \longrightarrow (FeH^+)_{ads}$$

$$(FeH^+)_{ads} + H^+ + ne^- \longrightarrow Fe + H_2$$
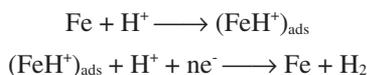
Adsorption isotherm: The interaction of the inhibitor molecules with the active sites on the metal surface can be described by the adsorption isotherms. Several adsorption isotherms such as Langmuir, Freundlish, Temkin and Frumkin were tested. In present work Langmuir adsorption isotherm gave the best description of the adsorption behaviour of wood tar inhibitor.

$$\frac{C_{Inh.}}{\Theta} = \frac{1}{K_{ads}} + C_{Inh.} \qquad (5)$$

where $C_{inh.}$ is the inhibitor concentration, Θ is the degree coverage of the sample surface and K_{ads} is the adsorption process equilibrium constant. Plot of C/Θ *versus* $C_{inh.}$ (Fig. 6) gives a straight line with regression coefficient R^2, approximately equal to 1.0. This suggests that the adsorption of *Olea europaea* subsp. *Cuspidata* wood tar on mild steel surface in H_2SO_4 solution obeys Langmuir adsorption isotherm. The standard free energy of adsorption ($\Delta G°_{ads}$) was calculated using the following equation [56]:

$$K_{ads} = \frac{1}{C_{H_2O}} \exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad (6)$$

$$-\Delta G°_{ads} = -2.303 \, RT \log (55.55 K_{ads}) \qquad (7)$$

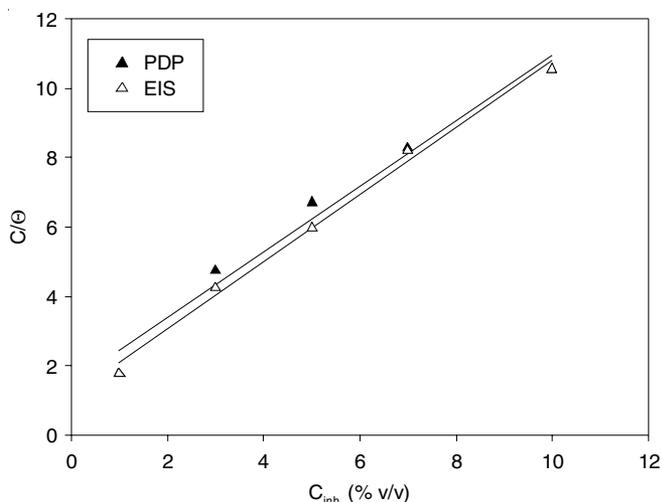where C_{H_2O} is the molar concentration of water molecules at the interface between the electrode surface and the solution

Fig. 6. Langmuir isotherms plots for adsorption of *Olea europaea* subsp. *Cuspidata* wood tar oil at 30 °C

and $\Delta G°_{ads}$ is the standard free energy, R universal gas constant is equal to 8.314 J mol^{-1} and T temperature in Kelvin.

The values of $\Delta G°_{ads}$ and K_{ads} of investigated wood tar inhibitor are calculated and recorded in Table-3. The negative value of $\Delta G°_{ads}$ indicates that the adsorption process of inhibitor molecules on mild steel surface is spontaneous process.

TABLE-3
THERMODYNAMIC PARAMETERS FOR ADSORPTION OF
Olea europaea subsp. *Cuspidata* WOOD TAR OIL ON
STEEL IN 1 M H_2SO_4 SOLUTION AT 30 °C

Method	Slope	K_{ads} (M^{-1})	Linear regression coefficient	$-\Delta G_{ads}$ (kJ mol^{-1})
PDP	1.48	1.057	0.977	10.261
EIS	1.10	1.030	0.993	10.196

Conclusion

In this study the results showed that:

• Wood tar oil of *Olea europaea* subsp. *Cuspidate,* determined by using PDP, EIS and SEM measurements at concentration (1-10 % v/v) and it can acts as an effective corrosion inhibitor for mild steel in 1.0 M H_2SO_4 containing 10 % EtOH.

• The maximum inhibition efficiency was 94.97 % at 10 % v/v of the extract.

• Compatibility between the inhibition efficiencies obtained from different techniques (PDP & EIS).

• The inhibition of corrosion is due to the adsorption of active molecules in the wood tar inhibitor on the surface of mild steel sample and blocking the active regions, it was characterized by the decrease in:

(i) polarization resistance (R_p) for the solutions in the presence of inhibitor, (ii) current densities ($I_{corr.}$) observed from PDP curves carried out in the presence of *Olea europaea* subsp. *Cuspidata* wood tar oil, (iii) double-layer capacitance (C_{dl}) calculated from EIS experiments.

• SEM images illustrated that the irregularities in the surface due to corrosion is absent in the inhibited surface and the surface is almost free from corrosion.

• The experimental results fit Langmuir adsorption isotherm from both PDP and EIS measurements.

• Standard free energy values ($\Delta G°_{ads}$) for the adsorption of *Olea europaea* subsp. *Cuspidate* wood tar oil have a negative value which indicates that the adsorption of inhibitor molecules on mild steel surface is spontaneous.

• The results showed that *Olea europaea* subsp. *Cuspidate* Wood tar oil acts as an excellent anticorrosion for mild steel in H_2SO_4 acid.

Advantages of research: The advantages of *Olea europaea* subsp. *Cuspidata* wood tar oil are several. It have all-natural ingredients, cost significantly lower, safe (non-toxic) it is liquid at room temperature and thus easier to use in any formulation. We here show that this extract also function as astonishing corrosion inhibitor for metals without any neutralization of the acids.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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