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Green Approach to Corrosion Inhibition of Mild Steel in SulphuricAcid Solution by the Extract of Olea europaea L. Leaves

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Abstract

The inhibitive behaviour of the extracts of olive (*Olea europaea L.*) leaves against corrosion of mild steel in H_2SO_4 medium was researched by using electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The temperature's effect on the corrosion behaviour of mild steel was also investigated. The adsorption characteristics of the olive leaves extracts were determined by utilizing the obtained data. The surface morphology of mild steel was examined after its exposure to 1M H_2SO_4 free and containing 50 g L^{-1} OLE solutions by scanning electron microscopy (SEM). Also, surface characterization was done on the mild steel exposed to 1 M H_2SO_4 solution with 50 g L^{-1} OLE by Fourier transform infrared spectroscopy (FT-IR). Results obtained from several measurement techniques revealed that OLE was an effective inhibitor.

1. Introduction

Mild steel has widespread applications in industry owing to its low cost and high availability. However, it is easily corroded especially in acid solutions. Acid solutions are used in many industrial processes including pickling, chemical cleaning and processing and oil well acidification [1]. Due to the corrosive effects of acidic media, inhibitors are widely used to improve the resistance of metal against corrosion.

Most of the organic compounds are known as effective inhibitors for mild steel [2, 3]. The inhibition action of them is often linked to the presence of π electrons and heteroatoms such as N, S, O in the molecule [4-7]. These compounds are adsorbed on the metallic material and cover the active surface corrosion sites, hence reducing the corrosion rate. However, most of them are costly and have serious damage to the environment. Therefore, it is necessary to develop other corrosion inhibitors which are inexpensive and environmentally friendly. Natural products such as plant materials having such properties have received a high interest recently as corrosion inhibitors [8]. So, many recent researches have been made on them. These studies have shown that the leaf extracts of Salvia officinalis, Sansevieria trifasciata, Occimum viridis, Phyllanthus amarus, Murraya koenigii, Colocasia esculanta are efficient inhibitors in acidic solutions [9-17]. Although the olive tree is native to the Mediterranean region, it is grown in tropical and central Asia and various parts of Africa. Olive leaves have been used for both medicinal and nutritional uses in various cultures. They contain phenolic compounds including oleuropein, hydroxytyrosol, tyrosol, luteolin, rutin, caffeic acid, catechin and apigenin. Oleuropein ($C_{25}H_{32}O_{13}$) is the main phenolic compound of olive leaves [18-22]. The chemical structure of oleuropein is given in Figure 1.

The objective of this study is to search the inhibition abilities of the olive leaf extract as a type of green inhibitor for corrosion of mild steel in H_2SO_4 solution. The inhibitor effect of OLE was studied by applying EIS, potentiodynamic polarization measurements.

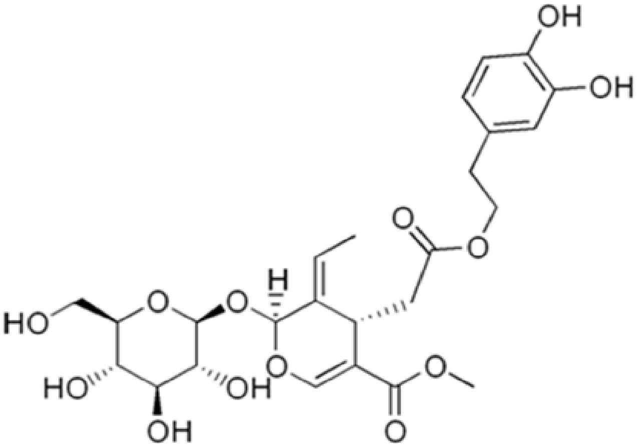


Figure 1: Chemical structure of *oleuropein*

2. Material and Methods

Olea europaea L. leaves were collected at Mersin, Turkey. Leaf samples were dried, powdered into small pieces, and then an amount of 10 g ground sample was extracted with 200 mL of 1 M H_2SO_4 (Merck) during 120 minute. The sample was filtered and adjusted to 200 mL of volume. The test solutions were prepared using the resultant stock solution.

The electrochemical studies were performed by using a three-electrode cell. The cell consisted of a mild steel as the working, a silver chloride (Ag/AgCl) as the reference and a platinum sheet (with 1 cm^2 surface area) as the counter electrode. A cylindrical rod of mild steel in a polyester block with exposure surface of 0.2 cm^2 was used. The chemical composition (wt. %) of the mild steel was given in Table 1. Prior to each measurement, the working electrode was polished with 400, 800, 1200 grades of emery papers and washed in distilled water. All electrochemical measurements were made with a computer controlled electrochemical analyser Gamry ZRA. The surface characterizations of the electrodes were done using SEM (Zeiss /Supra) and FT-IR (Perkin Elmer, Frontier) instruments. Infrared spectra were recorded in the wavenumber range of 400-4000 cm^{-1}.

Corrosion tests were carried out in 1 M H_2SO_4 solutions without and with various concentrations (5, 12.5, 25 and 50 g L^{-1}) of OLE. The frequency range for EIS measurements was 100 kHz to 10 mHz with an a.c. voltage amplitude of 5 mV. EIS data were fitted to appropriate circuits. Potentiodynamic polarization curves were recorded after EIS measurements at various temperatures (25-55 ^{0}C).

Table 1: The chemical composition (wt. %) of the mild steel

C	Mn	Si	P	S	Fe
0.125-0.30	0.57-0.62	0.03	0.012-0.018	0.039-0.045	remainder

3. Results and discussion

3.1. Potentiodynamic polarization measurements

Polarization curves for mild steel in 1 M H_2SO_4 solution without and with of 50 g L^{-1}OLE are given in Figure 2. Related corrosion kinetic parameters obtained from the polarization curves such as corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), anodic and cathodic Tafel slopes (b_a and b_c), and inhibition efficiencies (IE_1%) are given in Table 2. The IE_1 (%) was calculated using the following equation:

$$IE_1(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \qquad (1)$$

where i_{corr} and i'_{corr} are the current densities without and with OLE, respectively. It is clear from Figure 2 that E_{corr} shifts to more positive values in the presence of OLE. The addition of OLE to the aggressive solution inhibits the corrosion of mild steel affecting more than cathodic reaction than anodic. Furthermore, b_c values decreased as OLE concentration increased. The b_c value is decreased from 10.78 for blank solution to 6.09 V dec^{-1} at the highest concentration of OLE studied. As can be seen from Figure 2, both anodic and cathodic current densities were decreased in the presence of OLE. This confirmed that OLE inhibited both anodic metal dissolution of iron and cathodic hydrogen evolution reaction. The presence of OLE doesn’t remarkably change the corrosion potential. Therefore, it can be concluded that OLE behaves as mixed-type inhibitor. The inhibition efficiency reaches a maximum value (99 %) in the presence of 50 g L^{-1} OLE. The high inhibition efficiency of OLE is probably caused by the formation of an adherent and compact inhibitor film on the mild steel. This protective film diminishes the active sites exposed to the aggressive medium.

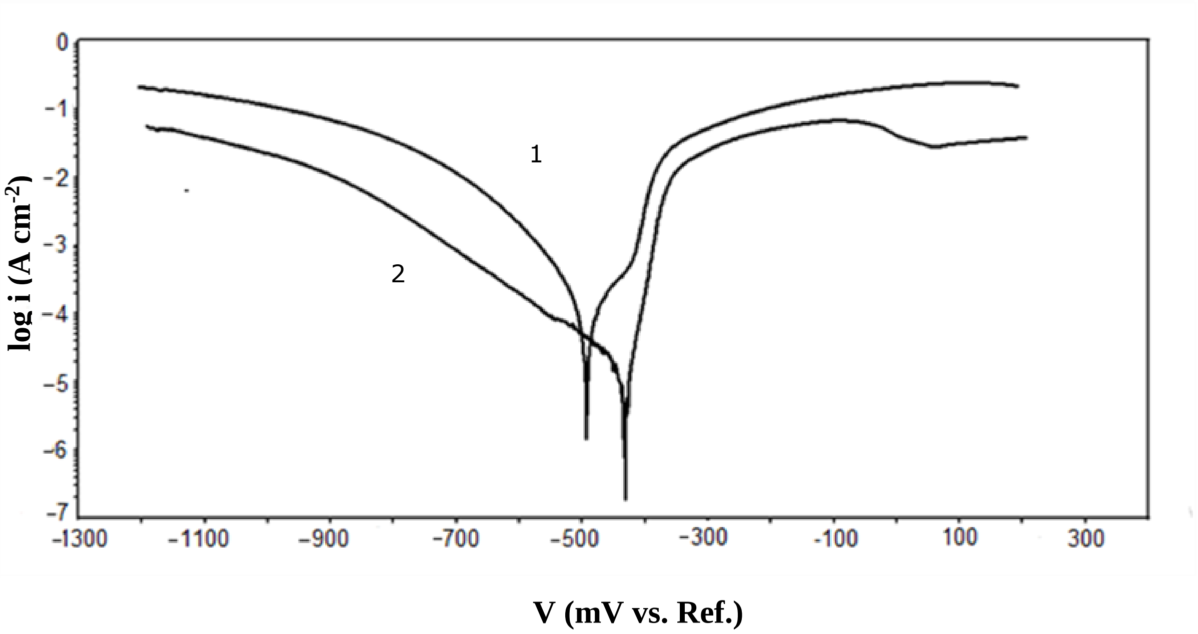


Figure 2: Polarization curves for mild steel in 1M H_2SO_4 solution in absence (1) and presence of 50 g L^{-1}OLE (2)

Table 2: Corrosion parameters obtained from the polarization curves in 1 M H_2SO_4 solution in the absence and presence of OLE

C(g L^{-1})	*E_{cor}(mV)*	*i_{corr}(mA cm^{-2})*	*b_a(dec V^{-1})*	*b_c(dec V^{-1})*	*R_p (Ω)*	*IE_1%*
Blank	-493	1.4×10^{-1}	11.93	10.78	144	–
5	-442	1.8×10^{-5}	23.97	7.21	499	90
12.5	-420	1.5×10^{-5}	42.25	6.67	626	92
25	-423	1.2×10^{-5}	47.22	6.11	733	98
50	-432	1.1×10^{-5}	46.03	6.09	810	99

3.2. Effect of temperature

Potentiodynamic polarization curves obtained in the temperature range of 25-55 ^{0}C in 1 M H_2SO_4 solution with 50 g L^{-1} OLE are shown in Figure 3. In acid solution containing 50 g L^{-1} OLE, the corrosion currents of mild steel increase with the increase in temperature. The number of the adsorbed molecules decreases thus the inhibition efficiency of OLE diminishes. Despite this behaviour, OLE indicates satisfactory inhibiting efficiencies even at higher temperatures (90 % at 55 ^{0}C) (Table 3).

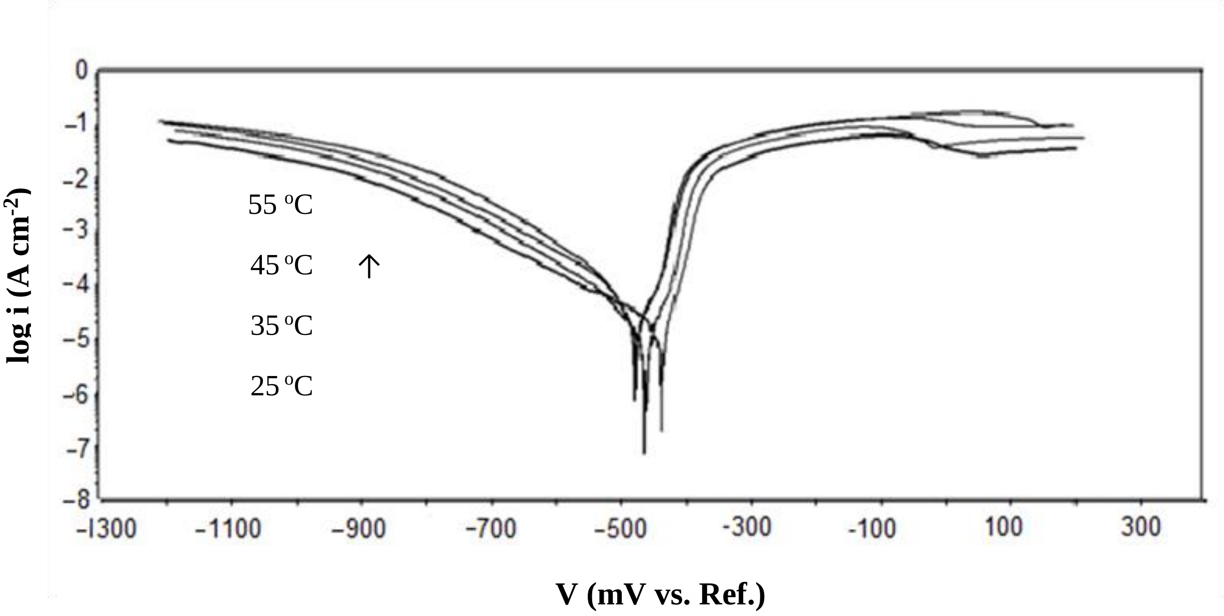


Figure 3: Polarization curves obtained at various temperatures in 1 M H_2SO_4 solution with 50 g L^{-1} OLE

Table 3: Corrosion parameters obtained from the polarization curves in the temperature range of 25-55 ^{0}C in 1 M H_2SO_4 solution in the absence and presence of 50 g L^{-1} OLE

Temp. (ºC)	*1M H_2SO_4*		*1M H_2SO_4 + 5O g L^{-1} OLE*		
	Ecorr (mV)	*i_{corr}(mA cm^{-2})*	*E_{corr}(mV)*	*i_{corr}(mA cm^{-2})*	*IE_1*
25	- 493	1.4×10^{-1}	-432	1.1×10^{-5}	99
35	-476	2.0×10^{-1}	-454	1.5×10^{-5}	95
45	-475	5.4×10^{-1}	-472	2.3×10^{-5}	92
55	-472	1.1×10^{-0}	-474	2.7×10^{-5}	90

The activation energy can be calculated from Arrhenius equation:

$$\ln i_{corr} = \ln A - \frac{E_a}{RT} \qquad (2)$$

where i_{corr} is the corrosion rate, Ea the activation energy, R is the molar gas constant, T the absolute temperature, and A is the frequency factor. Figure 4 shows the Arrhenius plots in 1 M H_2SO_4 solution without and with addition of 50 g L^{-1}OLE. The Ea values were found to be 57.13 kJ mol^{-1} and 24.89 kJ mol^{-1} in uninhibited and inhibited solutions. The lowered activation energy obtained with the addition of OLE could be related to its chemisorption on the steel surface [23].

3.3. Electrochemical impedance spectroscopy

Figure 5 shows Nyquist plots obtained from electrochemical impedance measurements in 1 M H_2SO_4 solution without and with different concentrations (from 5 to 50 g L^{-1}) of OLE after 1h exposure time. Nyquist plots display single depressed semi-circles whose diameter increased by increasing the concentration of OLE. The deviation of semicircles from ideal circles is related to impurities and heterogeneity of solid surfaces [24]. The semi-circular appearance shows that the corrosion process of mild steel is charge transfer controlled. In uninhibited H_2SO_4 solution, a small loop was also observed at low frequencies. This behaviour is generally attributed to the adsorption of the accumulated species at the metal electrolyte interface [25].

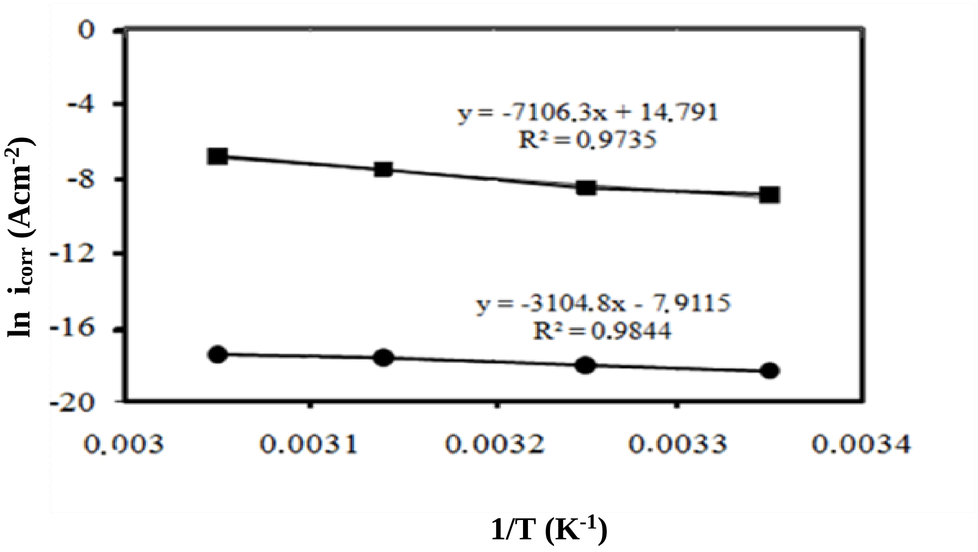


Figure 4: Arrhenius plots obtained in 1 M H_2SO_4 solution without (■) and with addition of 50 g L^{-1} OLE (●)

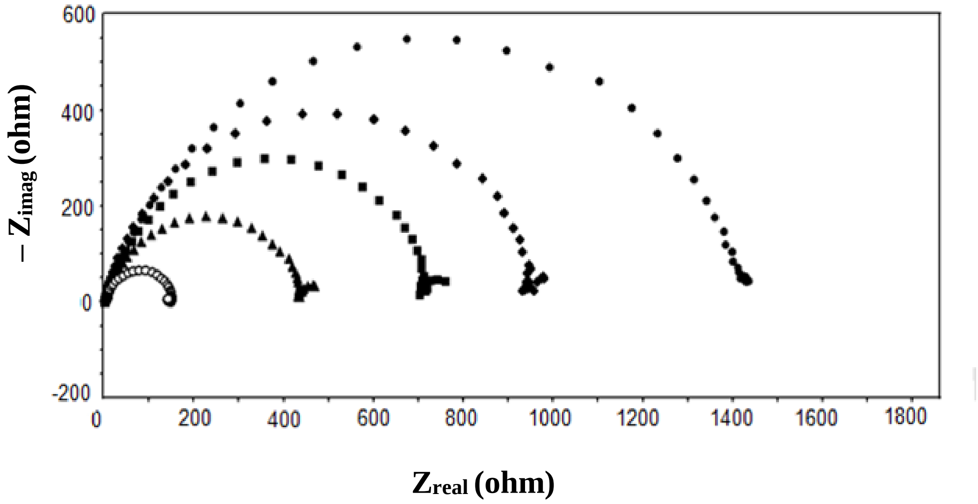


Figure 5: Nyquist plots after 1h of immersion time for mild steel in 1 M H_2SO_4 solutions in the absence and presence of different concentrations of OLE, (o) blank (▲) 5 g L^{-1} (■) 12.5 g L^{-1} (♦) 25 g L^{-1} (●)50 g L^{-1}

The inhibitive behaviour of OLE was tested for 120 h period in 1 M H_2SO_4 solution with 50 g L^{-1} OLE using EIS (Fig. 6). It can be seen from Figure 6 that the diameter of semicircles decreases with increasing in time. This can be related to degradation of surface film. However, the percent inhibition efficiency was 96 % even 120 h later in 1 M H_2SO_4 including 50 g L^{-1} of OLE (Table 4).

The obtained impedance data (Fig. 7a and b) was analysed by fitting in the adequate circuit models (Fig. 8a and b). In the equivalent circuits, R_s is the electrolyte resistance, CPE is the constant phase element, R_L is the inductor resistance, L is the inductance and R_p is the polarization resistance. R_p value of mild steel must be equal to the sum of the charge transfer resistance (R_{ct}), the diffuse layer resistance (R_d), the resistance of all accumulated species (R_a) and inductor resistance for blank solution [26]. In the case of the inhibited solution, R_p includes inhibitor film resistance (R_f) and pore resistance (R_{po}). Rpo is related to corrosion and diffusion process occurring within uncovered regions and pores [27].

The fitting parameters and percentage inhibition efficiency values are given in 1M H_2SO_4 free and containing 50 g L^{-1} OLE in Table 5. Inhibition efficiency was found to be 87 % after 1h of immersion. The adsorption of OLE on the metal surface decreases double layer capacitance because of the substitution process between OLE and the water molecule and other ions [28].

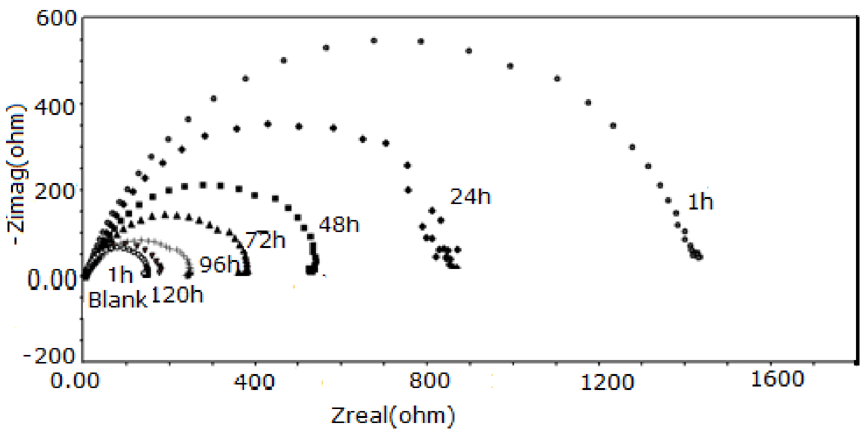
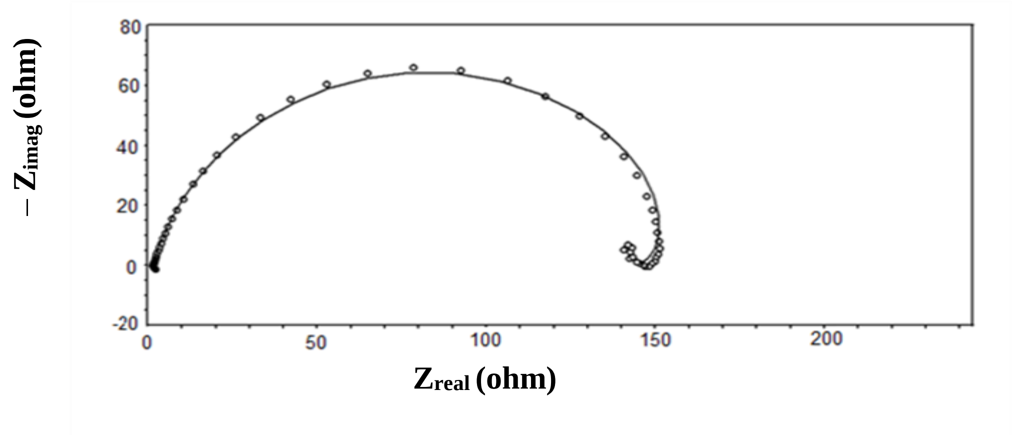


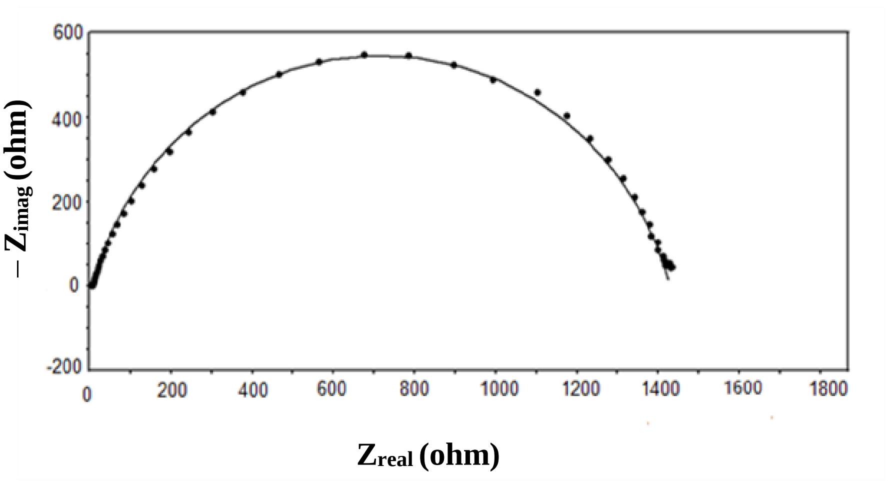
Figure 6: Nyquist plots after different immersion times for mild steel in 1 M H_2SO_4 solution in the absence (1h) and presence of 50 g L^{-1} OLE (1h, 24 h, 72 h, 96 h and 120 h)

Table 4: Polarization resistances obtained from the impedance measurements in 1 M H_2SO_4 solution in the absence and presence of 50 g L^{-1} OLE at various immersion times

Time (h)	*1M H_2SO_4*	*1M H_2SO_4 + 5O g L^{-1} OLE*	
	R_p(Ω)	**R_p(Ω)**	**IE_2%**
1	141	1430	94
24	81	868	90
48	26	527	94
72	14	360	96
96	10	237	95
120	7	177	96

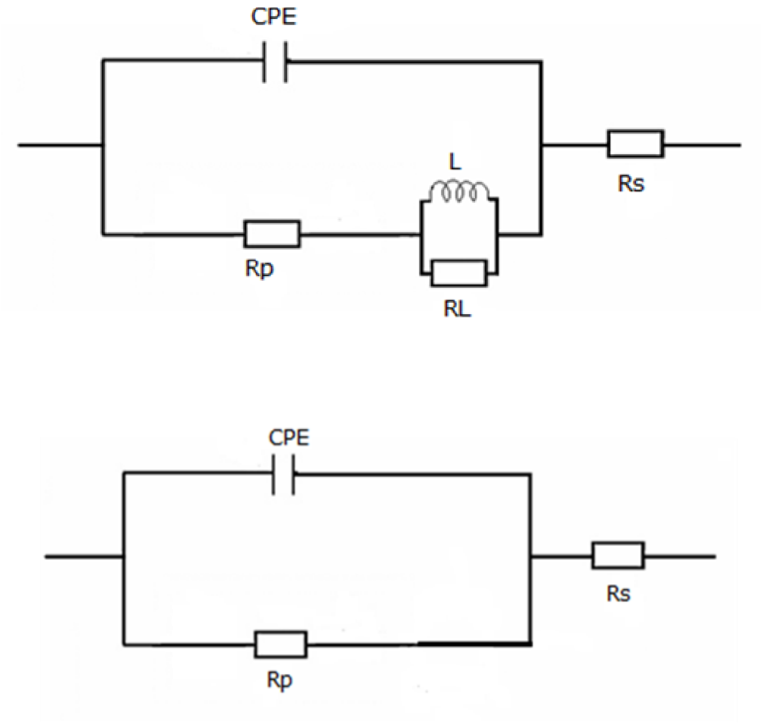


(a)



(b)

Figure 7: Nyquist diagrams for mild steel in 1 M H_2SO_4 in the absence **(a)** and presence of 50 g L^{-1}OLE **(b)** after 1h immersion time, solid lines show fitted data using equivalent circuit



(a)

(b)

Figure 8: The equivalent circuit model for corrosion process of mild steel in 1 M H_2SO_4 in the absence **(a)** and presence of 50 g L^{-1} OLE **(b)**

Table 5. Fitting results of impedance spectra for the corrosion of the mild steel in 1 M H_2SO_4 solution in the absence and presence of 50 g L^{-1} OLE

Solution	***Rs (Ω)***	***CPE₁ (F)***	***n_1***	***R_L (Ω)***	***L(H)***	***Rp (Ω)***	***IE_2 %***
1 M H_2SO_4	1.58	2.94×10^{-6}	0.86	163.5	400.2	156	_
1MH_2SO_4 + 50 g L^{-1} OLE	5.9	72.2×10^{-6}	0.83	_	_	1453	87

3.4. Adsorption isotherm

The inhibition ability of OLE is proportional to the surface coverage (θ) values. In order to obtain knowledge about the adsorption behaviour of OLE, the variation of θ with the OLE concentration must be obtained. It has been preferred to evaluate the adsorption process using EIS because the sine wave perturbation of 5 mV amplitude does not disturb the surface. The values of θ were calculated by the
Eq.3

$$\theta = \frac{Rp^{-1} - Rp(inh)^{-1}}{Rp^{-1}} \qquad (3)$$

where R_p and $R_{p\ (inh)}$ are the polarization resistances without and with OLE, respectively. Langmuir, Frumkin and Temkin adsorption isotherms were tested to describe the adsorptive behaviour of OLE on mild steel in H_2SO_4 solution. Temkin isotherm was found more suitable with an average correlation coefficient of 0.9505 (Fig. 9). The Temkin adsorption isotherm can be expressed as [29]:

$$\log\left(\frac{\theta}{c}\right) = \log K - g\theta \qquad (4)$$

where θ is the surface coverage, Kads is the adsorption equilibrium constant, C is the inhibitor concentration and g is the adsorbate interaction parameter. The value of the free energy (ΔG) of adsorption wasn't calculated because the value of ΔG depends on the proportions of the various components in OLE.

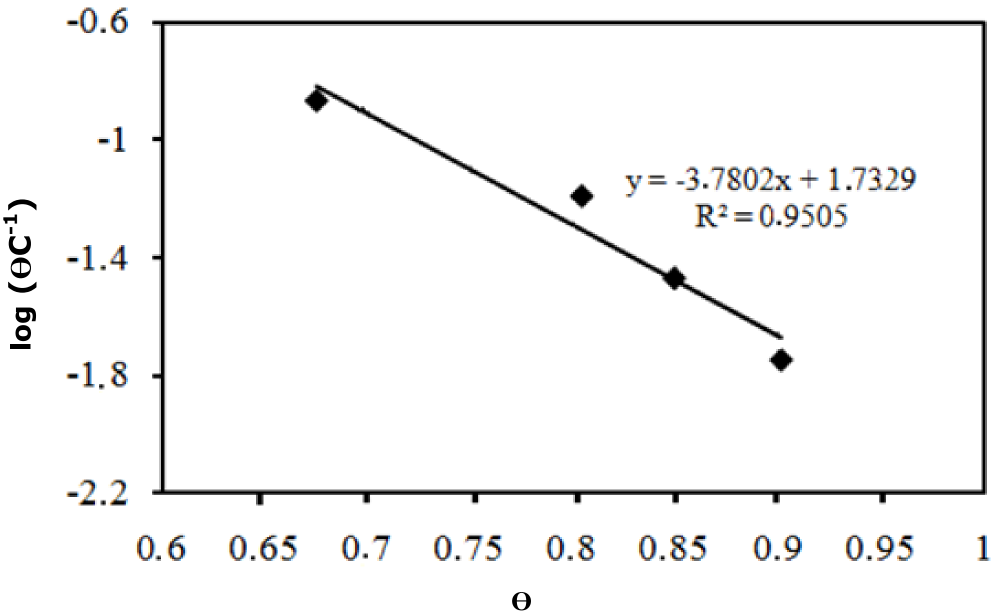


Figure 9: Temkin adsorption plot for the mild steel electrode in 1 M H_2SO_4 containing different concentrations of OLE

Oleuropein, the main component of olive leaf extract, contains many O atoms in functional groups and O-heterocyclic rings. This main compound might be protonated in acid media. Its adsorption depends mainly on the nature and surface charge of metal, the charge of inhibitor, the adsorption mode and electrolyte. It is reported that the surface of steel in H_2SO_4 solution is positively charged [30, 31]. In that case, the acid anions of SO_4^{2-} could be firstly adsorbed on steel surface. Then, the protonated inhibitor molecules may adsorb on the negatively charged metal.

The following reaction steps are proposed for anodic dissolution of mild steel in H_2SO_4 solution.

- $Fe + SO_4^{-2} \leftrightarrow (FeSO_4^{-2})_{ads}$ (step a)

- $(FeSO_4^{-2})_{ads} \leftrightarrow FeSO_4 + 4e^-$ (step b)

The cathodic hydrogen evolution reaction occurs on mild steel during the corrosion process in acidic environment as below:

- $H^+ + e^- \leftrightarrow H_{ads}$
- $H^+ + H_{ads} + e^- \leftrightarrow H_2$

The protonated organic molecules can be adsorbed on the metal surface by the electrostatic interactions with already adsorbed SO_4^{-2} ions (Fe $SO_4^{-2}{}_{ads}$)(Step a) . Thus, the $FeSO_4$ formation (Step b) is inhibited and anodic dissolution of mild steel is reduced [32, 33]. Then the protonated inhibitor molecules form a protective layer on the mild steel surface as follows:

$$Fe^{2+} + mH_2O + nSO_4^{-2} + p(Ekst)^+ \leftrightarrow [Fe(Ekst)_p(OH)_m(SO_4)_n]^{2-m-2n+p} + mH^+$$

The non-protonated molecules in the OLE may be adsorbed to the metal surface according to the following reaction.

$$Fe^{2+} + mH_2O + nSO_4^{-2} + p(Ekst) \leftrightarrow [Fe(Ekst)_p(OH)_m(SO_4)_n]^{2-m-2n} + mH^+$$

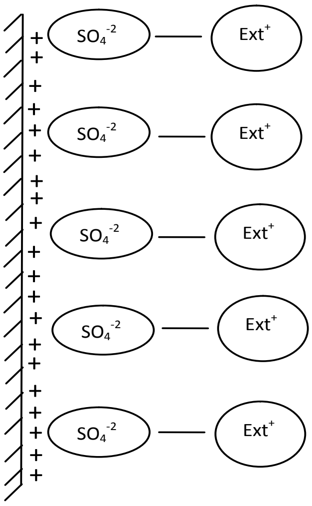


Figure 10: Schematic representation of adsorption of the OLE to the mild steel surface in the sulphuric acid solution

Besides, as the OLE contains so many components, the inhibition action may be due to synergistic interactions of the active molecules of this extract.

3.5. Scanning Electron Microscopy (SEM)

SEM micrographs of the mild steel surfaces exposed to 1M H_2SO_4 solution without and with the 50 g L^{-1} OLE after seven days are shown in Figure 11. In the absence of OLE, the SEM images revealed that the mild steel surface strongly damaged due to corrosive attack by the acid solution. However, it is clearly seen from Figure10b that a protective film was formed on the steel surface in the presence of OLE and the surface became smooth, with almost no pits and cracks.

3.6. FT-IR Analysis of Mild Steel Surface

FT-IR spectrum (Fig.12) was obtained after treatment of mild steel surface with highest concentration of inhibitor solution. A wide peak has been seen in the range of 3000-3500 cm^{-1}. It is attributed to stretching vibrations of an O–H and N–H. The peak seen at 1637 cm^{-1} belongs to C=O stretching vibrations.

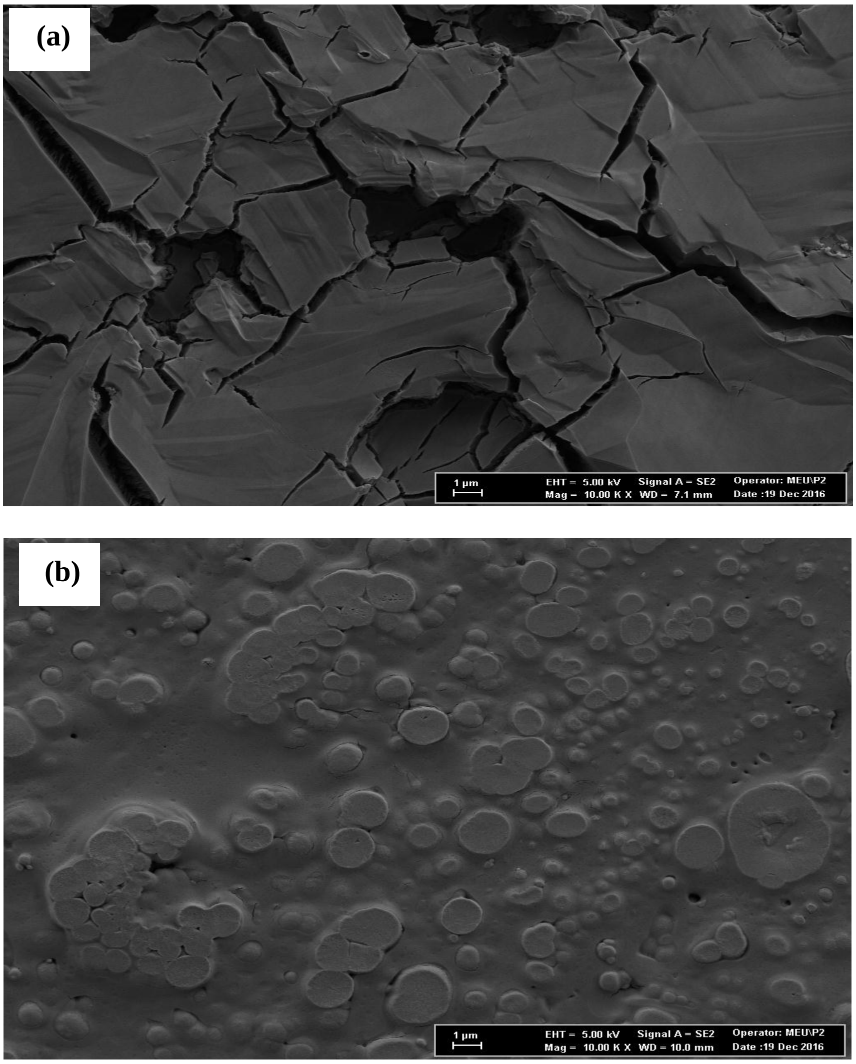


Figure 11: SEM images of mild steel surfaces after exposing to 1 M H_2SO_4 solution for seven days in the absence **(a)** and presence of 50 g L^{-1}OLE **(b)**

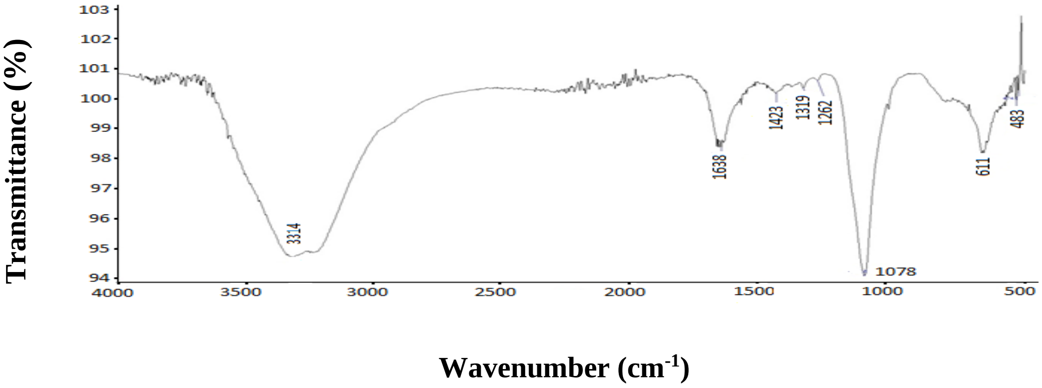


Figure 12: FT-IR spectrum obtained after treatment of mild steel surface in 1 M H_2SO_4 in the presence of 50 g L^{-1}OLE.

Also, C–O (alcohols, ethers, carboxylic acids, esters) and C–N stretching (amines, amide) vibrations give strong bands 1300-1050 cm^{-1} and 1360-1180 cm^{-1}, respectively [34]. The peak at about 610 cm^{-1} is the C=C out of plane bending vibrations of aromatic ring [35]. Infrared results show that olive leaves extract includes several organic compounds having O–H, N–H, C=O, C–N, C=C functional groups.

Conclusion

OLE showed a good inhibitive effect on the corrosion of mild steel in 1 M H_2SO_4. The addition of OLE to the 1 M H_2SO_4 solution modified the corrosion process of mild steel in the temperature range of 25-55 ^{0}C. The highest percent inhibition efficiency was 96% even 120 h later in 1 M H_2SO_4 including 50 g L^{-1} of OLE. The adsorption of OLE on the mild steel fitted Temkin isotherm.

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References

1. F. Bentiss, M. Lebrini, H. Vezin, M. Lagrenee, Experimental and theoretical study of 3-pyridyl-substituted 1,2,4-thiadiazole and 1,3,4-thiadiazole as corrosion inhibitors of mild steel in acidic media, *Mater. Chem. Phys.* 87 (2004) 18-23. https://doi.org/10.1016/j.matchemphys.2004.05.040
2. M. V. Fiori-Bimbi, P. E. Alvarez, H. Vaca, C. A. Gervasi, Corrosion inhibition of mild steel in HCL solution by pectin, *Corros. Sci.* 92 (2015) 192-199. https://doi.org/10.1016/j.corsci.2014.12.002
3. M. Düdükcü, G. Avcı, Corrosion inhibition of 4-aminoquinaldine on mild steel in acid media, *Res. Chem. Intermed.* 41 (2015) 4861-4871. https://doi.org/10.1007/s11164-014-1572-2
4. G. Avcı, Y. Keleş, Aqueous extract of Acacia cyanophylla leaves as environmentally friendly inhibitor for mild steel corrosion in 1 M H_2SO_4 solution, *Surf. Interface Anal.* 43 (2011) 1311-1317. https://doi.org/10.1002/sia.3714
5. K. Singh, E. E. Ebenso, M. A. Quraishi, Corrosion inhibition behavior of cefuzonam at mild steel/HCl acid interface, *Res. Chem. Intermed.* 39 (2013) 3033-3042. https://doi.org/10.1007/s11164-012-0815-3
6. S. Hong, W. Chen, H. Q. Luo, N. B Li, Inhibition effect of 4-amino-antipyrine on the corrosion of copper in 3 wt.% NaCl solution, *Corros. Sci.* 57 (2012) 270-278. https://doi.org/10.1016/j.corsci.2011.12.009
7. G. Quartarone, L. Ronchin, A.Vavasori, C. Tortato, L. Bonaldo, Inhibitive action of gramine towards corrosion of mild steel in deaerated 1.0 M hydrochloric acid solutions, *Corros. Sci.* 64 (2012) 82-89. https://doi.org/10.1016/j.corsci.2012.07.008
8. C. Verma, E. E. Ebenso, I. Bahadur, M. A. Quraishi, An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media, *J. Mol. Liq.* 266 (2018) 577-590. https://doi.org/10.1016/j.molliq.2018.06.110
9. R. Fuchs-Godec, G. Zerjav, Corrosion resistance of high-level-hydrophobic layers in combination with Vitamin E–(α-tocopherol) as green inhibitor, *Corros. Sci.* 97(2015)7-16. doi.org/10.1016/j.corsci.2015.03.016
10. Y. J. El-Etre, Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves, *J Colloid Interface Sci.* 314 (2007) 578-583. https://doi.org/10.1016/j.jcis.2007.05.077
11. L. Li, X. Zhang, J. Lei, J. He, S. Zhang, F. Pan, Adsorption and corrosion inhibition of Osmanthus fragran leaves extract on carbon steel, *Corros. Sci.* 63 (2012) 82-90. https://doi.org/10.1016/j.corsci.2012.05.026.
12. N. Soltani, N. Tavakkoli, M. Khayatkashani, M. R. Jalali, A. Mosavizade, Green approach to corrosion inhibition of 304 stainless steel in hydrochloric acid solution by the extract of Salvia officinalis leaves, *Corros. Sci.* 62- (2012) 122-135. https://doi.org/10.1016/j.corsci.2012.05.003
13. E.E. Oguzie, Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract, *Corros. Sci.* 49 (2007) 1527-1539. https://doi.org/10.1016/j.corsci.2006.08.009
14. E.E. Oguzie, Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel, *Corros. Sci.* 50 (2008) 2993-2998. https://doi.org/10.1016/j.corsci.2008.08.004
15. P. C. Okafor, M. E. Ikpi, I.E. Uwah, E. E. Ebenso, U. J. Ekpe, S. A. Umoren, Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media, *Corros. Sci.* 50 (2008) 2310-2317. https://doi.org/10.1016/j.corsci.2008.05.009
16. M.A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, S. K. Ashish, Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves, *Mater. Chem. Phys.* 122 (2010) 114-122. https://doi.org/10.1016/j.matchemphys.2010.02.066
17. H.F. Chahul, T. B. Danat, R.A. Wuana, Corrosion Inhibition Studies on the Influence of Colocasia esculenta Leaves Extract on Mild Steel in 1.0 M HCl, *J. Mater. Environ. Sci.* 10 (2019) 266-273. http://www.jmaterenvironsci.com/Document/vol10/vol10_N3/28-JMES-Chahul-2019.pdf

18. B. Le Toutour, D. Guedon, Antioxidative activities of Olea europaea leaves and related phenolic compounds, *Phytochemistry,* 31 (1992) 1173-1178. https://doi.org/10.1016/0031-9422(92)80255-D
19. C. Rahal, M. Masmoudi, R. Abdelhedi, R. Sabot, M. Jeannin, M. Bouaziz, P. Refait, Olive leaf extract as natural corrosion inhibitor for pure copper in 0.5 M NaCl solution: A study by voltammetry around OCP, *J. Electroanal. Chem.*769 (2016) 53-61. https://doi.org/10.1016/j.jelechem.2016.03.010
20. P. Xie, L. Huang, C. Zhang, Y. Zhang, Phenolic compositions, and antioxidant performance of olive leaf and fruit (Olea europaea L.) extracts and their structure–activity relationships, *J. Funct. Foods* 16 (2015) 460-471. https://doi.org/10.1016/j.jff.2015.05.005
21. O. Benavente-Garcıa, J. Castillo, J. Lorente, A. Ortuño, J.A. Del Rio, Antioxidant activity of phenolics extracted from Olea europaea L. leaves, *Food Chem*. 68 (2000) 457-462. https://doi.org/10.1016/S0308-8146(99)00221-6
22. M. Bouaziz, S. Sayadi, Isolation and evaluation of antioxidants from leaves of a Tunisian cultivar olive tree, *Eur. J. Lipid Sci. Technol.* 107 (2005) 497-504. https://doi.org/10.1002/ejlt.200501166
23. Ahamad, R. Prasad, M. A. Quraishi, Experimental and theoretical investigations of adsorption of fexofenadine at mild steel/hydrochloric acid interface as corrosion inhibitor, *J Sol. State Electrochem*. 14 (2010) 2095-2105. https://doi.org/10.1007/s10008-010-1041-9
24. G. W. Walter, A review of impedance plot methods used for corrosion performance analysis of painted metals, *Corros. Sci*. 26 (1986) 681-703. https://doi.org/10.1016/0010-938X(86)90033-8
25. T. Tüken, B. Yazıcı, M. Erbil, Zinc modified polyaniline coating for mild steel protection, *Mater. Chem. Phys*. 99 (2006) 459-464. https://doi.org/10.1016/j.matchemphys.2005.11.023
26. G. Kardaş, R. Solmaz, Electrochemical Investigation of Barbiturates as Green Corrosion Inhibitors for Mild Steel Protection, *Corros. Rev*. 24 (2006) 151-172.https://doi.org/10.1515/CORRREV.2006.24.3-4.151.
27. R. Solmaz, G. Kardaş, M. Çulha, B. Yazıcı, M. Erbil, Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media, *Electrochim. Acta* 53 (2008) 5941-5952. https://doi.org/10.1016/j.electacta.2008.03.055
28. M. H. Hussin, M. J. Kassim, The corrosion inhibition and adsorption behavior of Uncaria gambir extract on mild steel in 1 M HCl, *Mater. Chem. Phys.* 125 (2011) 461-468. https://doi.org/10.1016/j.matchemphys.2010.10.032
29. F.S. Souza, A. Spinelli, Caffeic acid as a green corrosion inhibitor for mild steel, *Corros. Sci.* 51 (2009) 642-649. https://doi.org/10.1016/j.corsci.2008.12.013
30. A.K. Satpati, P.V. Ravindran, Electrochemical study of the inhibition of corrosion of stainless steel by 1,2,3-benzotriazole in acidic media, *Mater. Chem. Phys.* 109 (2008) 352-359. https://doi.org/10.1016/j.matchemphys.2007.12.002
31. F. Bentiss, M. Traisnel, M. Lagrenee,The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media, *Corros. Sci.* 42 (2000) 127-146. https://doi.org/10.1016/S0010-938X(99)00049-9
32. A. Döner, R. Solmaz, M. Özcan, G. Kardaş, Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution, *Corros. Sci.* 53 (2011) 2902-2913. https://doi.org/10.1016/j.corsci.2011.05.027
33. A. K. Satapathy, G. Gunasekaran, S. C. Sahoo, K. Amit, P.V. Rodrigues, Corrosion inhibition by *Justicia gendarussa* plant extract in hydrochloric acid solution, *Corros. Sci.* 51 (2009) 2848-2856. https://doi.org/10.1016/j.corsci.2009.08.016
34. S. Trassati, Work function, electronegativity, and electrochemical behaviour of metals: II. Potentials of zero charge and "electrochemical" work functions, *J. Electroanal. Chem. Interf. Electrochem.* 33 (1971) 351-378. https://doi.org/10.1016/S0022-0728(71)80123-7
35. D. Skoog, J. J. Leary, Principles of Instrumental Analysis, 4th ed., Fort Worth Saunders College Pub. ISBN: 0030233437 (1992).

(2020) ; http://www.jmaterenvironsci.com