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Oleaster leaf extract: a potential environmentally friendly inhibitor for mild steel

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Abstract: In this research, the potential of *Elaeagnus angustifolia* tree leaf extract as a green corrosion inhibitor for mild steel in hydrochloric acid solution was examined. The stock concentration of the aqueous extract was determined to be 0.38% (w/v). Other experimental solutions were created by diluting four different extract concentrations in aggressive solution. Experimental measurements, including linear polarization (LPR), electrochemical impedance spectroscopy (EIS), and semi-logarithmic current potential curves by Tafel extrapolation method, were employed to validate the corrosion inhibition effects of the plant leaf extract at varying concentrations. Notably, oleaster leaf extract demonstrated a corrosion protection of over 90% for 0.018% w/v concentration on the mild steel, attributed to its abundance in secondary metabolites such as polyphenols and flavonoids. The atomic force microscopy (AFM) surface maps provide robust evidence for the electrochemical measurement data.

Keywords: *Elaeagnus angustifolia*, Environmentally-friendly inhibitor, Acidic corrosion, AFM.

1. Introduction

Corrosion is an inherent and independent process wherein pure metals and their alloys undergo transformation into various stable forms, such as sulfides, oxides, hydroxides, and more. This occurs through chemical and/or electrochemical reactions with the surrounding environments (Singh et al., 2016a; Verma et al., 2018). Corrosion poses a detrimental threat to the assets of various traffic and railway bridges, buildings, industries as well as households. Due to its correlation with significant economic and safety losses, corrosion stands as a critical issue that demands attention from scientists and engineers engaged in the field of corrosion discipline and engineering worldwide (Haque et al., 2017). Numerous corrosion prevention methods have been developed, among which the use of green corrosion inhibitors has gained popularity as one of the most accessible and economical approaches. This is attributed to their ease of access and application, as well as their high effectiveness even at relatively low concentrations (Singh et al., 2016b; Ramezanzadeh et al., 2015).

Indeed, the use of conventional corrosion inhibitors is currently constrained as a result of the growing emphasis on "green chemistry" in the realms of engineering, technology, and science. "Green chemistry" is indeed a discipline of scientific and technological exploration that operates on a series of principles with the primary goal of minimizing the release of environmentally harmful substances into the surroundings. This approach entails both the design and application of chemicals that are ecofriendly (Mohammadinejad et al., 2016). The consideration given to the development of green corrosion inhibitors has also extended to the utilization of various plant extracts, pharmaceuticals, and ionic liquids. Plants exhibit a distinctive ability to transform solar energy into life-sustaining organic compounds like carbohydrates through the procedure of photosynthesis (Alibakhshi et al., 2018; El-Hajjaji et al., 2018). They also serve as a natural source for numerous raw materials, including fruits, wood, vegetables, oils, dyes, and resins, which have various commercial applications in our everyday lives.

Elaeagnus angustifolia L., the effect of which was investigated in this study, is a deciduous shrub or small tree with a rich botanical history, habitually referred to as Russian olive, Persian olive or Wild olive. With distinctive silvery-green foliage and small fragrant flowers, *Elaeagnus angustifolia* has not only captivated the attention of botanists but also played a significant role in various cultural and ecological contexts (Zhang et al., 2023).

Elaeagnus angustifolia, a member of the Elaeagnaceae family, stands out for its remarkable adaptability, thriving across a diverse array of environmental conditions. As the adverse effects of traditional corrosion inhibitors become more apparent, there is a growing emphasis on sustainable alternatives, particularly those aligned with the principles of "green chemistry". In this context, natural plant extracts have emerged as promising candidates for corrosion inhibition.

This study delves into the potential of *Elaeagnus angustifolia* plant extract as a green corrosion inhibitor for mild steel in acidic environment. *Elaeagnus angustifolia*, also known as Oleaster, is a deciduous shrub renowned for its adaptability and unique biochemical composition. The investigation focuses on the inhibitory effects of the plant extract on mild steel corrosion, exploring its efficiency, mechanism, and viability as an eco-friendly alternative. This research is notable as there is no previous study in the literature demonstrating the utilization of oleaster species' leaf extract as an inhibitor to impede metallic corrosion. This study also aims to provide a different perspective on the developing capacity of this plant leaf extract as an acidic environment green inhibitor for the first time.

2. Materials and Method

2.1. The aqueous extract solutions of Elaeagnus angustifolia leaves

A quantity of approximately 15 g of dried *Elaeagnus angustifolia* leaf (Figure 1) was placed into a 250 mL reaction flask and subjected to reflux for 24 hours with the addition of sufficient distilled water. Following the 24-hour reflux process, the extract was filtered, resulting in an approximate volume of 180 mL with an orange colour. The concentration of the stock solution derived from *Elaeagnus angustifolia* leaf was determined to be 0.380% (w/v). Various other concentrations were prepared by dilution from this stock solution.

Fig. 1 The photograph of dried *Elaeagnus angustifolia* leaves

After preparing the stock solution, the concentrations employed for electrochemical experiments were varied, ranging from the highest concentration to the lowest at 0.18%, 0.09%, 0.05%, and 0.02% (w/v), respectively. Figure 2 illustrates a schematic reflux procedure of *Elaeagnus angustifolia* leaf to enhance the clarity of the study. Conducting experiments in a 1.0 M HCl (hydrochloric acid) solution, known for its aggressive nature, enables the examination of electrochemical behaviour.

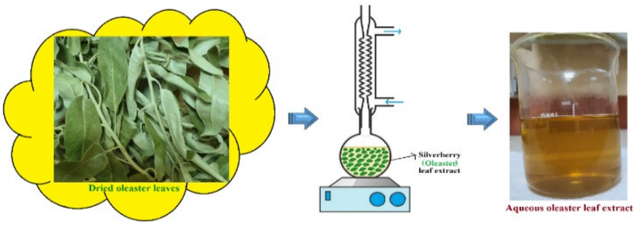

Fig. 2 Schematic of *Elaeagnus angustifolia* leaf extraction procedure

2.2. Preparation of materials

The chemical composition of mild steel, whose corrosion behaviour was studied as a working electrode, is presented in Table 1. These electrodes were introduced into a cylindrical mould that contained polyester, the mild steel surface area in communication with the electrolyte solution was 0.5024 cm^2. Before being put into use, the test electrodes underwent polishing using sandpaper with grits of 150, 600, and 1000. Afterward, the electrode surfaces were meticulously cleansed with distilled water and acetone. A three-electrode system was used in experiment measurements. The initial electrode employed was the mild steel as working electrode. The second electrode, functioning as the counter electrode, was composed of a platinum plate with a surface area of 2.0 cm^2. The final electrode employed was Ag/AgCl (3.0 M KCl), utilized as the reference electrode. All potentials documented in this investigation are calibrated with respect to this electrode.

Table 1 The chemical composition of the mild steel electrodes

Element	%	Element	%	Element	%
(C)	0.08400	(Si)	0.10200	(Mn)	0.40900
(P)	0.01100	(S)	0.01900	(Cr)	0.06030
(Mo)	0.01040	(Ni)	0.07890	(Al)	Trace
(Co)	0.00198	(Cu)	0.21700	(Nb)	0.00222
(Ti)	Trace	(V)	0.01100	(W)	Trace
(Pb)	Trace	(Sn)	0.01620	(Sb)	Trace
(Fe)	Remain				

EIS, LPR and Tafel extrapolation experiments were used to try-out the anti-corrosion property of *E. angustifolia* leaf extract for mild steel in HCl environment via the CHI660B electrochemical workstation. Throughout the open circuit potential (E_{ocp}=E_{corr}), the mild steel electrodes were soaked in the testing solution for 1h at 298 K until the iron surface extends a temporary stable state. When conducting EIS measurement, the starting potential was a balanced E_{ocp} value, and the method frequency limit was from 100000 Hz to 0.005 Hz with 5.0 mV amplitude signal. The LPR limit of the polarization curve is E_{ocp} -0.010 V to E_{ocp} +0.010 V and the potentiodynamic polarization by Tafel extrapolation method were documented at cathodic potential of -0.350 V and anodic potential of +0.350 V with reference to E_{corr}, respectively. This procedure was executed at a scanning rate of 1.0 mV s^{-1}. Surface survey was seized over the course of 1h in an electrolyte HCl solution, both with and without *E.*

angustifolia leaf extract, utilizing the AFM technique (Veeco Multimode 8 Nanoscope 3D model).

3. Results and Discussion

3.1. EIS, LPR and Potentiodynamic polarization findings

EIS measurement is appropriate for quickly, accurately, and efficiently gathering data on metal corrosion rates. It can be efficiently employed to evaluate the inhibitor under investigation's anti-corrosion characteristics (Tan et al., 2021). As EIS is conducted using alternating current, it is recognized for its non-damaging effect on the metal surface. The inhibitory effect of *E. angustifolia* leaf extract on the iron surface, characterized by a green inhibitory impact, was examined using EIS, LPR, and potentiodynamic polarization methods during a 1h immersion time at 298 K across four (0.02%-0.18% w/v) concentrations. In this process, two sets of electrical equivalent circuit models were studied; Figure 3 for aggressive 1.0 M HCl and Figure 4 for the extract solutions. The equivalent circuits for the corrosion and inhibition processes were derived from the EIS data with the assistance of Zview2 software.

In Figures 3 and 4, notable distinctions between the two proposed circuits are apparent. Especially in solutions that contain *E. angustifolia* leaf extract, a clear inhibitor film develops on the mild steel surface, leading to a concurrent rise in resistance. Figure 4 offers a more lucid understanding, depicting that the introduction of *E. angustifolia* leaf extract in different concentrations to the acidic solution results in a decrease in mild steel electrode corrosion. It is performed as the *E. angustifolia* leaf extract adheres to the mild steel surface, forming a preventive film layer that efficiently impedes corrosion. Furthermore, the impedance diagrams in Figure 4 clearly illustrates the augmented diameters of the capacitive loops in direct correlation with the enhance in *E. angustifolia* leaf extract concentration (Mert and Doğru Mert, 2023).

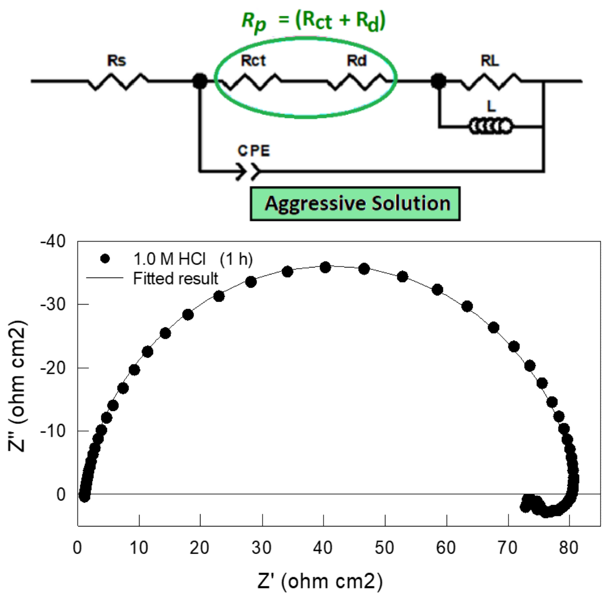

Fig. 3 Electrical circuit recommended and impedance diagram in aggressive solution for 1h

The relevant experiment parameters are succinctly presented in Table 2. The impedance plots exhibit two distinct frequency regions: the high-frequency region corresponds to the diffuse layer (R_d) and charge transfer (R_{ct}) in the corrosion exposure process (Karazehir et al., 2022). The low-frequency field is the locus of inhibition, controlled by the film resistance (R_f) that develops on the mild steel surface, originating from the oleaster leaf extract. Moreover, two constant phase elements (*CPEs*) are evident in the process of oleaster leaf extract solution. The first signifies the double-layer capacitance (CPE_{dl}), while the second corresponds to the capacitance of the film layer on the mild steel (CPE_{film}).

Upon scrutinizing the polarization resistance values obtained from the EIS and *LPR measurements in Table 2, it became apparent that the inhibition efficiency values (η% and $^*\eta$%) significantly rose with the incorporation of the extract of *E. angustifolia* leaf into the aggressive solution. The inhibition efficiencies calculated from the findings of the EIS and LPR measurements ranged from 84.1% to 90.5% and 84.2% to 90.7%, respectively.

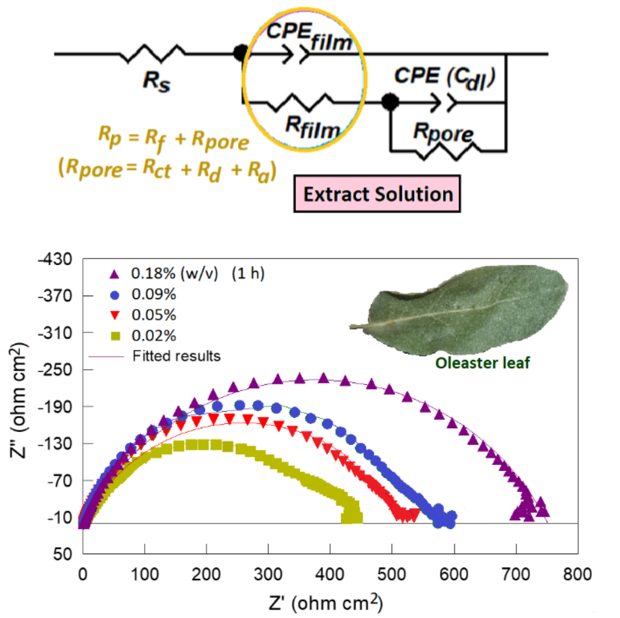

Fig. 4 Electrical circuit recommended and impedance curves in containing four concentrations of *Elaeagnus angustifolia* leaf extract

The *CPE* value obtained by the EIS method was determined as 110 µF/cm² for the aggressive solution. This value gradually decreased with increasing extract concentration and was obtained as 60 µF/cm² for the highest inhibitor concentration. The higher *CPE* in the inhibitor-free solution is explained by the higher number of diffused species in the absence of the inhibitor (Mert, 2022). In addition, the E_{corr} value of the aggressive medium was -0.474 V, and as oleaster leaf extract was added to the medium, it took on more negative potential values. The "*n*" value, which is described as the surface roughness coefficient in Table 2, also decreased as the inhibitor concentration increased. This is one of the indicators that the *E. angustifolia* leaf extract, whose inhibitory effect was examined, protects the mild steel by forming a film on its surface.

The **potentiodynamic polarization method by Tafel extrapolation, an alternative electrochemical technique, was outlined to determine the dissolution parameters of the mild steel, and the results are indicated in Table 2.

Figure 5 depicts the semi logarithmic current-potential curves of the test electrodes immersed in an HCl solution at 298 K, featuring four different concentrations of *E. angustifolia* leaf extract. It seems that as leaf extract is added to the electrolyte aggressive solution, current density values decrease and this decrease is more dominant in the cathodic curves (Nazlıgül et al., 2022). In this case, the inhibitor can be described as functioning as a cathodic inhibitor on the mild steel in the acidic environment (Akkoç et al., 2023). In Table 2, the corrosion current density value (i_{corr}) were 265 μA/cm² in acidic environment, but decreased to 25 μA/cm² in the presence of highest concentration of oleaster leaf extract, and the inhibition at this concentration was 90.6%.

There was no discernible difference between the solution with and without the inhibitor when assessing the cathodic Tafel constant ($-\beta_c$) values in Table 2. In this case, it was concluded that the hydrogen evolution mechanism was not affected by the oleaster leaf extract (Özkır, 2019). The results obtained by all three experimental methods were complementary and highly compatible with each other, and it was concluded that the adsorption of *E. angustifolia* leaf extract on the iron surface protected it by forming a film as a result of high inhibition. Moreover, since this extract does not have any toxic environmental effects, it is inevitable to be considered as a green inhibitor. EIS measurements were proved Tafel analysis.

Table 2 EIS, LPR and potentiodynamic polarization parameters from the experiments in solutions without and with *E. angustifolia* leaf extract

C (% w/v)	**EIS**							
Elaeagnus angustifolia leaf extract	E_{corr} (V/Ag/AgCl)	R_s (Ωcm²)	CPE (μF cm⁻²)	CPE n	R_L (Ωcm²)	L (H)	R_p (Ωcm²)	η (%)
Blank	-0.474	1.2	110	0.94	8	4	72	-
0.02	-0.527	1.2	100	0.72	-	-	452	**84.1**
0.05	-0.530	1.2	90	0.71	-	-	525	**86.3**
0.09	-0.530	1.3	82	0.71	-	-	580	**87.6**
0.18	-0.536	1.2	60	0.70	-	-	755	**90.5**
	***LPR**							
Elaeagnus angustifolia leaf extract	*E_{corr} (V/Ag/AgCl)		*R_p (Ω cm²)				*η (%)	
Blank	-0.475		71				-	
0.02	-0.532		448				**84.2**	
0.05	-0.533		520				**86.3**	
0.09	-0.530		575				**87.7**	
0.18	-0.538		760				**90.7**	
	****Potentiodynamic polarization**							
Elaeagnus angustifolia leaf extract	**E_{corr} (V/Ag/AgCl)		$-\beta_c$ (mV dec⁻¹)		i_{corr} (μA cm⁻²)			**η (%)
Blank	-0.475		108		265			-
0.02	-0.536		102		43			**83.8**
0.05	-0.536		99		37			**86.0**
0.09	-0.533		105		34			**87.2**
0.18	-0.542		104		25			**90.6**

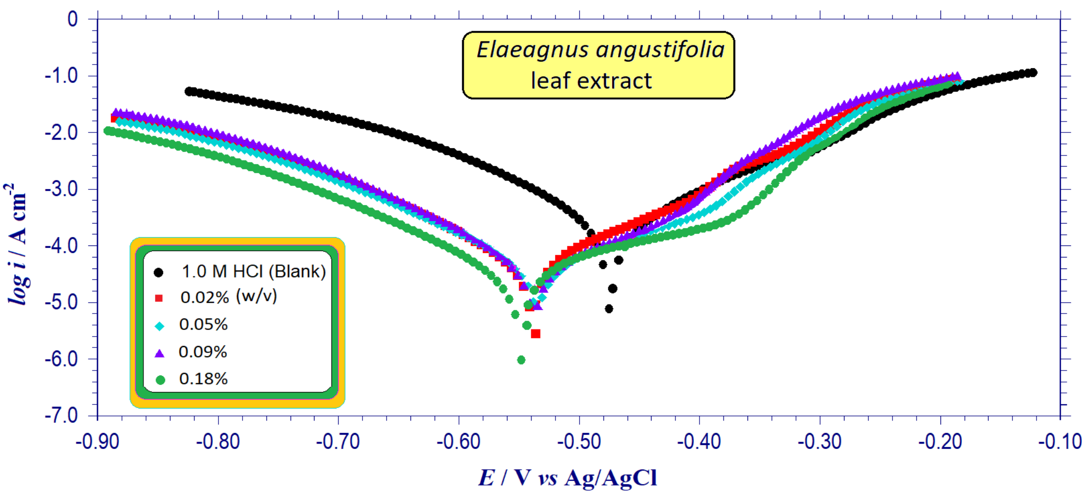

Fig. 5 Electrical circuit recommended and impedance diagram in aggressive solution for 1h

3.2. AFM analaysis

The detailed analysis with AFM further reinforced understanding of the surface mechanism of *E. angustifolia* leaf extract on mild steel. Figures 6 and 7 display three-dimensional images of the treated blank solution and 0.18% (w/v) extract solution for 1 hour.

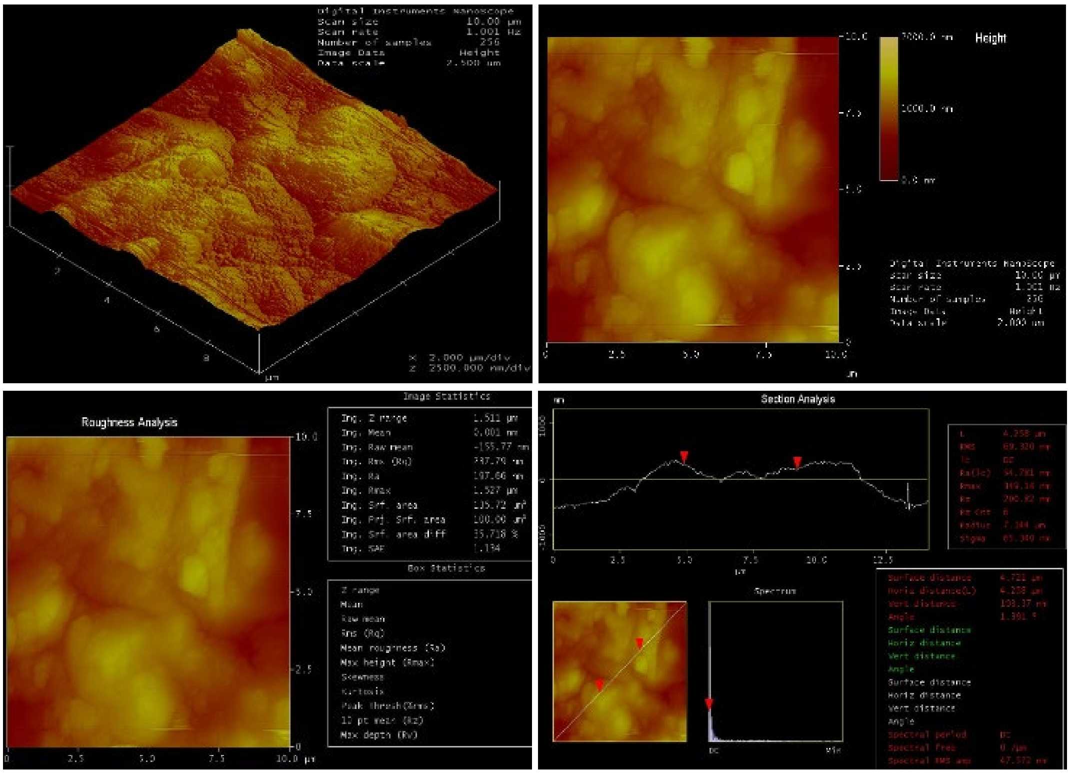

Fig. 6 AFM images of the mild steel in aggressive HCl solution for 1 h exposure

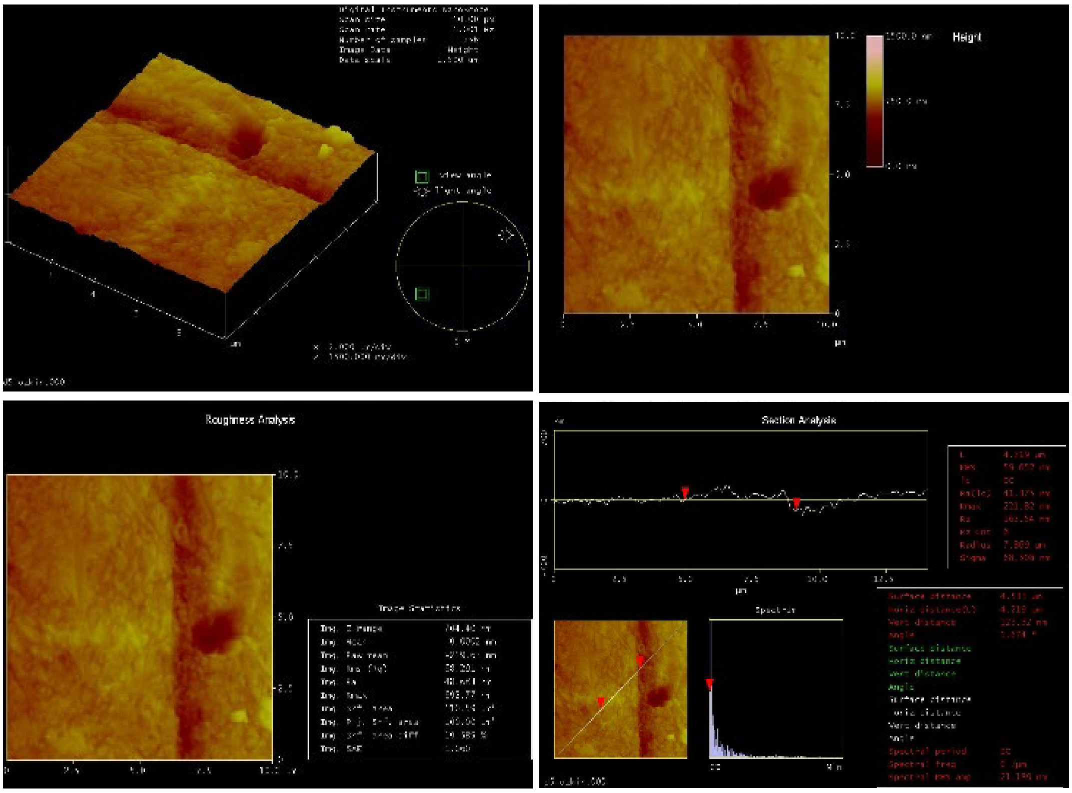

Fig. 7 AFM images of the mild steel with 0.18% (w/v) *E. angustifolia* leaf extract in HCl solution for 1 h exposure

Average surface roughness parameter (R_a) value for blank solution was determined as 197.66 nm. When the highest concentration of oleaster leaf extract was added to the solution, this value became 48.683 nm. The significant decrease in the average surface roughness value is further evidence that the green inhibitor used reduces the roughness of the metal in the acidic environment and that the inhibitor protects the surface of the mild steel. The results of the AFM analysis and electrochemical experimental measurements are quite consistent.

4. Conclusion

This paper is of great importance as it is the first application of the effect of aqueous *Elaeagnus angustifolia* leaf extract, from the Elaeagnaceae family, as a green and environmentally friendly inhibitor on the corrosion behavior of iron electrode in hydrochloric acid solution. The findings obtained with the three different methods applied were quite compatible with the surface analysis results.

The preservation of mild steel corrosion in 1 M HCl by the extract of *Elaeagnus angustifolia* leaves, acting as a green inhibitor, underscores the protective role of secondary metabolites present within the plant. The observed corrosion inhibition can be attributed to the rich composition of bioactive compounds inherent to oleaster leaves. These secondary metabolites, such as polyphenols, flavonoids, and tannins, are known for their anti-oxidative features, forming a resilient protective layer on the steel surface. The green inhibitor's efficacy in hindering corrosion emphasizes the potential of *Elaeagnus angustifolia* leaf extract as a promising and eco-friendly solution for corrosion mitigation in acidic environments.

Authors' contributions: DÖ, obtaining data & principle investigation & experimental measurements & editing & writing.

Conflict of interest disclosure: The author declares no conflict of interest on the written article.

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