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Research Article

INSIGHT INTO ANTI-CORROSION EFFECT OF *MAMMILLARIA PROLIFERA* FRUIT EXTRACT AS A GREEN INHBITOR FOR MILD STEEL IN HCl SOLUTION

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ABSTRACT

In this study, it was aimed to examine the adsorption and corrosion behaviours of the aqueous extract of *Mammillaria prolifera*, a cactus fruit, in 1.0 M HCl solution using experimental methods such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). *Mammillaria prolifera* is a cactus species from the Cactaceae family, commonly known as Texas nipple cactus. Experiments were realized for aqueous extracts of four different *Mammillaria prolifera* fruits. The results indicate that the aqueous extract solution of cactus fruit has outstanding anti-corrosive performance of over 90% at the optimum concentration of 0.120% (w/v). In addition to electrochemical experiments, FE-SEM surface images were taken as another indicator of high inhibition. The results showed that the mild steel surface immersed in the inhibited electrolyte solution at 298 K after one-hour exposure did not contain cracks, pits or deformations compared to the inhibitor-free surface. As a result, experimental measurements and FE-SEMsurface images support each other.

Keywords: *Mammillaria prolifera*, Green inhibitor, Adsorption, Mild steel, EIS.

1. INTRODUCTION

Corrosion, the gradual degradation of materials due to electrochemical reactions with their environment, poses a significant economic and safety challenge across various industries. Mild steel, widely employed as a structural material in various industrial applications, is favored for its combination of durability and workability [1]. However, when subjected to acidic environments, mild steel exhibits a high susceptibility to corrosion. Acidic corrosion poses a critical challenge, often leading to costly damage and functional impairment of steel structures. In industrial processes where acidic environments are prevalent, in energy production facilities, and in numerous sectors where chemical processes occur, mild steel structures are constantly exposed to acidic mediums [2]. This exposure accelerates the formation of rust layers on the steel surface, jeopardizing structural integrity. Therefore, comprehending the fundamental mechanisms of acidic corrosion and developing effective measures is of paramount importance to enhance the durability of soft steel structures and ensure their long-term viability [3].

To mitigate corrosion, numerous approaches have been explored, including the application of protective coatings, alloy modifications, and the use of corrosion inhibitors. The utilization of corrosion inhibitors, in particular, has garnered significant attention for its potential to impede or slow down corrosion processes [4]. This study will delve into the corrosion mechanisms of mild steel in acidic media and meticulously address the plant extract influencing this mechanism. Such environmentally friendly compounds, called green, contain elements in their structures that prevent corrosion and minimize the harmful effects of corrosion, as they contain aromatic rings that can bind and adsorb to the surface of the metal, and heteroatoms with double bonds and/or unpaired electron pairs [5,6].

Plant extracts, owing to their rich phytochemical composition, have emerged as promising candidates for corrosion inhibition. These extracts are abundant sources of secondary metabolites such as alkaloids, flavonoids, tannins, and phenolic compounds, which have demonstrated notable anti-corrosive properties in other laboratory settings [7,8]. The utilization of plant extracts as corrosion inhibitors not only presents an eco-friendly alternative to synthetic chemicals but also taps into the wealth of bioactive compounds that plants have evolved to defend against environmental stresses [9,10]. This paper aims to provide a comprehensive review of the current state of research on the utilization of plant extracts as corrosion inhibitors. By examining the inhibitory mechanisms and effectiveness of various plant-derived compounds, it was sook to contribute to the growing body of knowledge in corrosion science and offer insights into the potential practical applications of botanical extracts in corrosion control strategies.

Mammillaria prolifera, commonly known as the Texas Nipple cactus, is a species of cactus grown as an ornamental plant. While *Mammillaria prolifera* is primarily known for its distinctive cylindrical or globular shape and its ability to produce offsets (small new plants) prolifically, it is not typically cultivated for its fruit. However, like many cactus species, *Mammillaria prolifera* does produce small, fleshy fruits after flowering. These fruits are typically small, round, and may range in color from

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green to reddish, depending on the species and the degree of ripeness. The fruits of *Mammillaria prolifera*, like those of many cacti, are not typically consumed by humans and are not considered a significant part of the human diet [11].

In the light of this idea, in this study, the effect of *Mammillaria prolifera* fruit aqueous extract from the cactus species as an environmentally friendly green inhibitor on the corrosion of mild steel electrodes kept in 1.0 M HCl solution for one hour was investigated by two electrochemical methods. This study is also noteworthy because there is no previous study in the literature showing that this fruit extract of cactus species has been used as an inhibitor to inhibit metallic corrosion.

2. MATERIAL AND METHOD

2.1. The extract solutions of *Mammillaria prolifera* fruits

Mammillaria prolifera fruit, which was weighed about 10 g (Figure 1), was put into a 250 mL reaction flask and refluxed for 16 hours by adding enough distilled water. After 16 h of reflux process, the extract was filtered and its volume was approximately 120 mL. Its colour is light yellow. The concentration of the stock *M. prolifera* solution studied was calculated as 0.240% (w/v). Other concentrations were diluted from the stock solution. Following the preparation of the stock solution, the concentrations utilized for electrochemical experiments ranged from the highest concentration at 0.120% (w/v) to the lowest at 0.015% (w/v). These concentrations were established as 0.120% (w/v), 0.060% (w/v), 0.030% (w/v), and 0.015% (w/v), respectively, in order of decreasing strength. In Figure 2, a stereo-microscope image of the cactus fruit at a scale of 1000 μm is shown to make the study more understandable. Conducting experiments in a 1.0 M HCl (hydrochloric acid) solution allows for the study of electrochemical behaviour in an acidic medium.

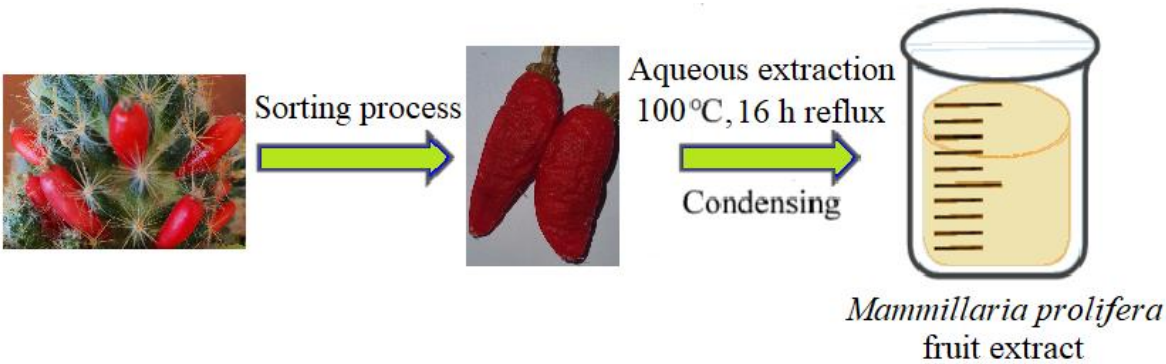

Figure 1. Schematic diagram for the preparation process of *M. prolifera* fruit extract.

Figure 2. Stereo microscope image of *M. prolifera* fruit.

2.2. Electrodes and electrochemical methods

The working electrode consisted of mild steel with the following weight percentage composition: 0.01100% P, 0.06030% Cr, 0.08400% C, 0.07890% Ni, 0.00222% Nb, 0.01100% V, 0.21700% Cu, 0.01040% Mo, 0.01900% S, 0.40900% Mn, 0.10200% Si, 0.01620% Sn, 0.00198% Co, and 98.977% Fe. These electrodes were inserted into a cylindrical mold containing polyester, exposing an area of 0.5024 cm² to the aggressive solution. The test electrodes were meticulously polished using abrasive paper with 150 and 600 grits. Subsequently, the electrode surfaces were thoroughly cleaned with acetone and distilled water. For electrochemical experiments, a three-electrode system was employed. The first electrode utilized was the mild steel working electrode. The latter electrode, serving as the counter electrode, consisted of a platinum plate with a surface area of 2.0 cm². The last electrode utilized was Ag/AgCl (3.0 M KCl), employed as the reference electrode. All potentials recorded in this study are referenced to the Ag/AgCl electrode.

Utilizing a computer-controlled CHI 660B model electrochemical analyser, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests were executed. These assessments were carried out in a 1.0 M HCl solution with and without four concentrations of *M. prolifera* fruit extract. Prior to commencing all electrochemical tests, the working electrodes were immersed in the working solution for one hour to ensure stabilization of the open circuit potential (E_{corr}) at 298 K. EIS experiments were conducted at the E_{corr}, encompassing a frequency range from 10^5 to $5x10^{-3}$ Hz, with a 5 mV amplitude applied to the system. The potentiodynamic polarization tests were registered at cathodic/anodic potentials of ±0.350 V relative to E_{corr}, respectively. This was performed at a scan rate of 1.0 mV s^{-1}. Surface analysis images were captured over the course of one hour in an aggressive solution (blank) both with and without *M. prolifera* fruit extract, employing the FE-SEM technique (Zeiss GeminiSEM 500 with computer control).

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurement findings

It is crucial that the chosen method for corrosion rate assessment minimally alters the innate structure of the metal surface. Hence, alternative current impedance, an electrochemical technique believed to exert minimal influence on the metal's nature, stands out as one of the most favoured approaches [12]. The inhibitory impact of *M. prolifera* fruit extract on the mild steel surface, exhibiting a green inhibitory effect, was assessed through EIS and potentiodynamic polarization methods during a one-hour immersion period at 298 K across four various concentrations. In this procedure, two sets of electrical equivalent circuit models were employed; Figure 3 for 1.0 M HCl and Figure 4 for the inhibited solutions. The corrosion and inhibition processes' equivalent circuits were derived from the EIS data with the aid of Zview2 software.

In Figures 3 and 4, it is evident that the two proposed circuits exhibit notable distinctions. Notably, for solutions containing *M. prolifera* fruit extract, a distinct inhibitor film forms on the mild steel surface, resulting in a corresponding increase in resistance. Figure 4 provides a clearer insight, illustrating that the addition of *M. prolifera* fruit extract in varying concentrations to the 1.0 M HCl solution leads to a reduction in mild steel electrode corrosion. This occurs as the *M. prolifera* fruit extract adsorbs onto the mild steel surface, creating a protective film layer that effectively hinders corrosion. Additionally, the EIS diagram in Figure 4 vividly portrays the increased diameters of the capacitive loops in direct correlation to the rise in *M. prolifera* fruit extract concentration.

The pertinent EIS and potentiodynamic polarization parameters have been summarized in Table 1. The impedance plots are characterized by two distinct frequency regions: the high frequency region pertains to the diffuse layer (R_d) and charge transfer (R_{ct}) in the corrosion process. The low frequency region is where inhibition occurs, governed by the film resistance (R_f) that forms on the mild steel surface, originating from the *M. prolifera* fruit extract. Additionally, two constant phase elements (*CPE*) are present in the cactus fruit extract solution process. The first represents the double layer capacitance (CPE_{dl}), while the second corresponds to the capacitance of the film layer on the mild steel (CPE_{film}). Upon examination of the polarization resistance values derived from the EIS measurements in Table 1, it was evident that the inhibition efficiency values ($\eta\%$) increased with the addition of the extract of cactus fruit to the aggressive solution. The inhibition efficiency values calculated from the results of the EIS method ranged from 88.6% to 91.4%. The capacitance value (CPE) in the blank solution measured at 110 $\mu F/cm^2$. However, it was observed that this value significantly increased when M. prolifera fruit extract was introduced into the HCl solution. The range of CPE values varied between 82–51 $\mu F/cm^2$. Additionally, the corrosion potential value (E_{corr}), initially at -0.474 V in the HCl electrolyte, shifted towards more cathodic potentials in solutions containing cactus fruit extract (refer to Table 1).

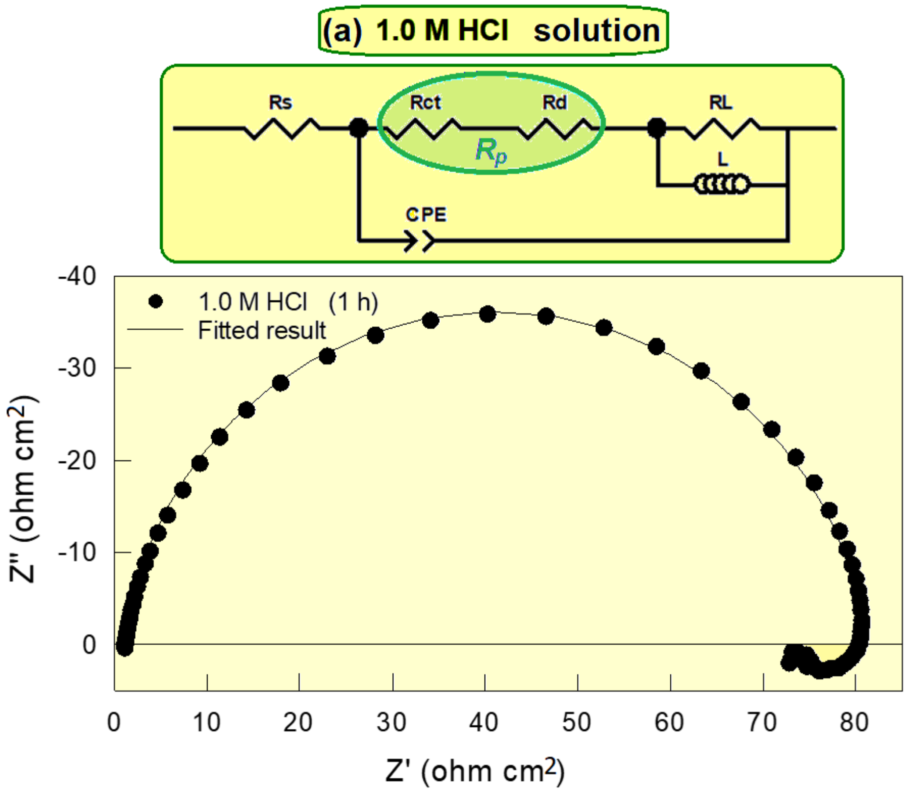

Figure 3. Electrical equivalent circuit proposed and EIS diagram for 1.0 M HCl solution after 1 h immersion.

The dissolution treatment parameters of the mild steel electrode, determined using the Tafel extrapolation method - an alternative electrochemical technique, are presented in Table 1.

Table 1. EIS and potentiodynamic polarization findings determined from the tests in solutions without and with *M. prolifera* fruit extract

***C* (w/v %)**	**EIS**							
***Mammillaria prolifera* fruit extract**	**E_{corr} (V/Ag/AgCl)**	**R_s (Ω cm^2)**	**CPE (μF cm^{-2})**	**CPE n**	**R_L (Ω cm^2)**	**L (H)**	**R_p (Ω cm^2)**	**η (%)**
1.0 M HCl	-0.474	1.2	110	0.94	8	4	72	-
0.015	-0.525	1.1	82	0.74	-	-	630	**88.6**
0.030	-0.531	1.2	71	0.70	-	-	700	**89.7**
0.060	-0.523	1.0	60	0.67	-	-	780	**90.8**
0.120	-0.522	1.3	51	0.65	-	-	840	**91.4**

***Mammillaria prolifera* fruit extract**	***Potentiodynamic polarization**			
	***E_{corr} (V/Ag/AgCl)**	**-β_c (mV dec^{-1})**	**i_{corr} (μA cm^{-2})**	***η (%)**
1.0 M HCl	-0.475	108	265	-
0.015	-0.526	102	33	**87.5**
0.030	-0.535	104	29	**89.1**
0.060	-0.525	100	25	**90.6**
0.120	-0.524	98	23	**91.3**

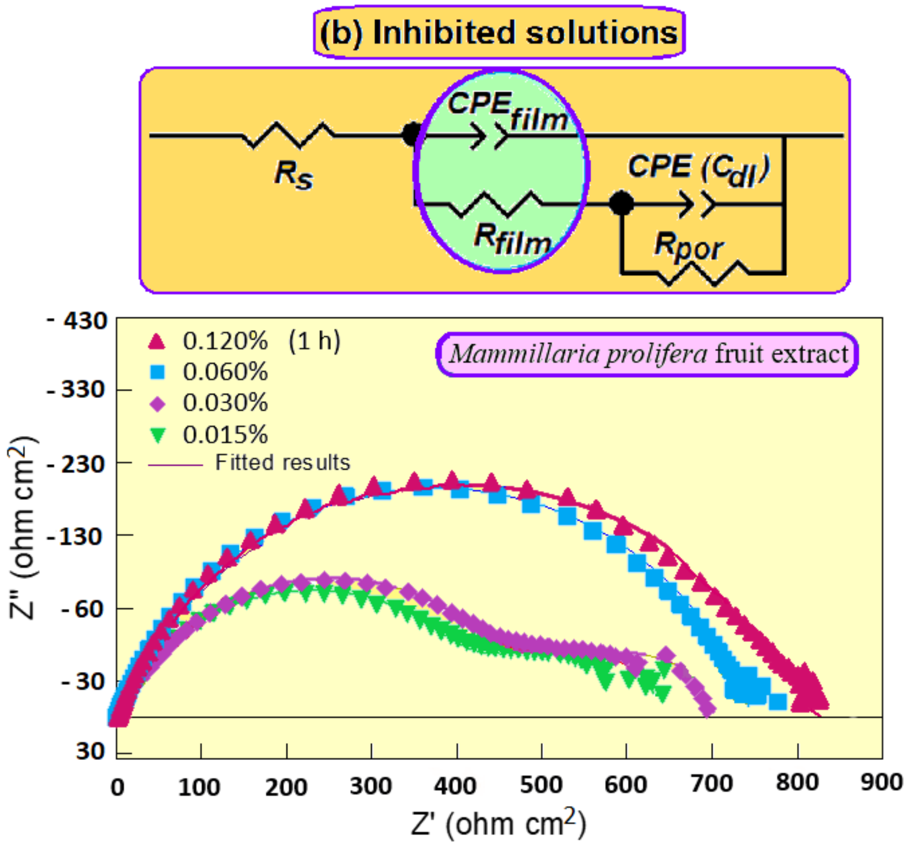

Figure 4. Electrical equivalent circuit proposed and EIS diagrams in containing different concentrations of *M. prolifera* fruit extract.

Figure 5 provides the potentiodynamic polarization plots for the working electrodes in HCl solution at 298 K, with four varying concentrations of *M. prolifera* fruit extract. In the absence of the extract, the corrosion current density (i_{corr}) measured 265 µA/cm². However, with the introduction of the cactus fruit extract into the HCl solution, these values gradually decreased.

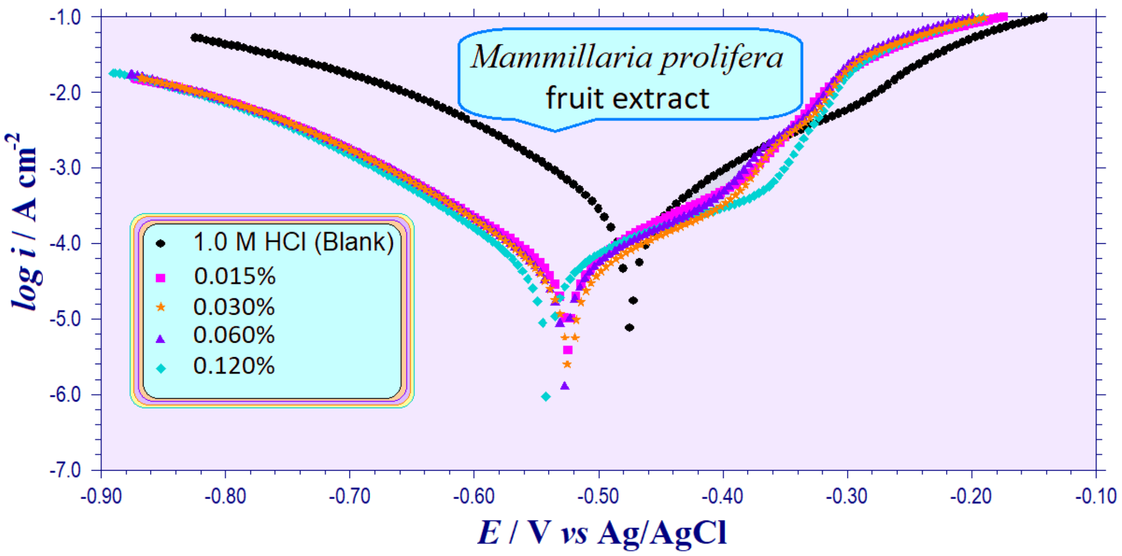

Figure 5. Potentiodynamic polarization plots of mild steels in HCl solution for four concentrations of *M. prolifera* fruit extract.

In all experimental solutions, as the concentration of *M. prolifera* fruit extract increased, corrosion current density (i_{corr}) values decreased, and inhibition efficiency values rose. While the cathodic Tafel constant ($-\beta_c$) was 108 *mV/dec* in the blank solution, it varied between 98 *mV/dec* and 104 *mV/dec* in the solutions with the inhibitor. The relatively stable cathodic Tafel constants across solutions with and without M. prolifera fruit extract suggest that the mechanism of hydrogen formation remained largely unaffected by the studied inhibitor. The semi-logarithmic current-potential curves and Table 1 collectively demonstrate that the $^{*}E_{corr}$ values, calculated by Tafel extrapolation of cathodic and anodic curves for the mild steel electrode at 298 K in an uninhibited solution, were recorded at -0.475 V. However, with the introduction of *M. prolifera* fruit extract solutions, the $^{*}E_{corr}$ values shifted towards more cathodic potentials.

Upon examining the cathodic plots depicted in Figure 5, it is evident that the addition of *M. prolifera* fruit extract led to a substantial reduction in current density within the 1.0 M HCl solution. This observation suggests that the *M. prolifera* fruit extract acted as a cathodic inhibitor in the 1.0 M HCl solution [13]. The findings obtained from both experimental methods complemented each other, leading to the conclusion that the adsorption of M. prolifera fruit extract on the metal surface is an inevitable phenomenon. Moreover, this extract can be considered a green inhibitor, as it does not have any adverse environmental effects.

3.2. Surface analysis by FE-SEM

Given that FE-SEM stands for field emission scanning electron microscope, it offers the capability to conduct surface analysis with significantly higher resolution, resulting in much clearer images [14]. Comprehensive surface analyses were conducted through FE-SEM analysis to elucidate the surface morphologies of mild steel electrodes that were immersed in 1.0 M HCl solutions, both with and without *M. prolifera* fruit extract at the highest concentration (0.120% w/v), at a constant temperature of 298 K for one hour. The FE-SEM morphologies are presented in Figure 6.

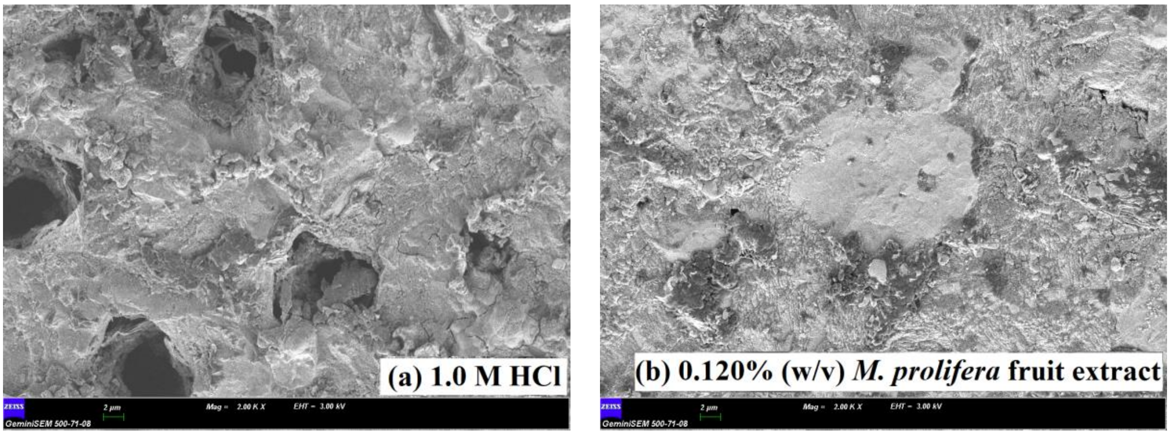

Figure 6. FE-SEM surfaces of the mild steels for 1 h exposure.

It was noted that the surface of the metal immersed in the solution without the inhibitor exhibited indentations and pit-like appearances. Conversely, the electrode immersed in the solution containing *M. prolifera* fruit extract appeared flatter, with a reduction in both the number and size of pits.

4. CONCLUSION

This study holds significance in first utilizing *M. prolifera* fruit extract from the Cactaceae family as an environmentally friendly and green inhibitor for mild steel in HCl solution. Through 1-hour exposure tests conducted by two different methods, it was observed that the M. prolifera fruit extract exhibited strong adsorption onto the mild steel surface, resulting in an inhibition rate of over 90% at its optimal concentration. The chemical composition of phytochemicals (secondary metabolites) present in M. prolifera fruit, characterized by aromatic rings, double bonds between phenolic groups, flavonoids, terpenoids, among others, plays a pivotal role in achieving such high inhibition efficiency against mild steel corrosion. This inhibitor effect, stemming from naturally derived, eco-friendly compounds, holds paramount importance for both industrial processes and the environment, given their biodegradable nature and absence of toxic components. The results obtained by the experimental method are quite consistent with the surface findings.

SIMILARITY RATE: 20%

AUTHOR CONTRIBUTION

Demet Özkır: Conceptualization, methodology, data curation, writing, editing etc.

CONFLICT of INTEREST

The author declares no conflict of interest.

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