



The Consistent Effect of *Citrus aurantium* Fruit Peels Extract as New Type Green Inhibitor on Mild Steel Corrosion in HCl Solution

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Abstract

The role of *Citrus aurantium* fruit peel extract solution in the existing research is to investigate the effect as corrosion inhibitor on mild steel in the atmospheric environment with its eco-friendly and green effect. It was studied the inhibitor effect of *Citrus aurantium* utilizing linear polarization (LPR), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The working electrodes were immersed in HCl solutions containing various concentrations of *Citrus aurantium* fruit peels extract in order to equilibrate the metal-solution interface for one hour before each measurement. The bitter orange fruit peels extract indicated a potent inhibitor influence as a consequence of one hour electrochemical tests, and with the raise of extract concentrations of *Citrus aurantium* fruit peels, the protection influence of mild steel electrodes in HCl solutions also enhanced. Finally, the surface morphologies of the working electrodes in aggressive HCl solutions without and with bitter orange fruit peels extract after one-hour immersion were analysed by an optical microscopy, it was concluded that the mild steel surface in the *Citrus aurantium* fruit peels extract solution had a flawless surface compared to the blank one. Experimental data and surface morphology results are highly consistent with each other.

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1 INTRODUCTION

Almost all metals are chemically unstable in air at ambient temperatures with some exceptions. Therefore, air and all aqueous environments are probable hostiles for metal [1, 2]. Especially in industrial applications, they need to be protected in order to achieve successful results. Corrosion is essentially a condition in which metal is vulnerable. It occurs when the protective mechanisms are deactivated, leaving the metal prone to any attack [3]. For this reason, it is very important to protect metals. Inhibitor applications are one of the most widely used corrosion inhibition techniques. Inhibitors are also very important in pickling processes, especially for surfaces such as mild steel [4]. The trend for green corrosion inhibitors has increased recently, as many organic inhibitors are toxic and not cost effective enough. Plant extracts, amino acids, vitamins are among the commonly used green corrosion inhibitors. Many studies have indicated that some vitamins act as good green corrosion inhibitors against steel under various types of media [5-7].

This study was carried out on the basis of whether the extract taken from the peels of the *Citrus aurantium* fruit, which is very rich in vitamin C, will act as a green inhibitor on the mild steel corrosion in an acidic medium. The taste of the bitter orange fruit, which looks like an orange, is sour and slightly bitter. Not only the fruit part itself, but also the leave and peel parts are another healing reservoir. Therefore, not only the fruit parts, but also the peel and even the leaves should be used. Bitter orange fruit has numerous benefits to the human body. While it contributes to the cleaning of the internal organs, it also ensures that the blood flows more cleanly [8, 9]. The peels of the bitter orange fruit used in this study, which are called phytochemicals and have a great importance in terms of health; It is known to contain organic substances rich in bioactive components such as polyphenolic compounds, flavonoids and carotenoids [10, 11]. The main feature of this fruit is that it has a thick peel and a rough outer surface. Therefore, the extract of the fruit peel was the main element in this study.

The objective of present study is to evaluate the effect of *Citrus aurantium* fruit peels extract in 1.0 M hydrochloride acid solution as a green inhibitor, the natural, green, cheap and environmentally safe, on mild steel corrosion by using electrochemical tests such as LPR, EIS and potentiodynamic polarization.

2 MATERIAL AND METHOD

2.1 Plant specimens

The *Citrus aurantium* specimens used in the study were collected from Adana, İmamoğlu, 83 m, 37°15'20" N, 35°39'07" E, in February, 06, 2022.

2.2 Preparation of the extract solutions of *Citrus aurantium* fruit peels

Chemicals tapped in electrochemical measurements are of analytical grade. Bitter orange samples were first washed and peeled. The bitter orange fruit peels were then cut into thin small particles. Approximately 60 g of *Citrus aurantium* fruit peels cut into small particles were placed in a 250 mL reaction flask, and enough purified water was added to it and refluxed for 16 h. The *Citrus aurantium* fruit peels extract was filtered after reflux process. The color of the filtrate obtained was orange. Figure 1 expresses the stages of extraction process. The stock concentration of bitter orange solution was defined as 4.651% (w/v) after 10 mL of the *Citrus aurantium* fruit peels extract was evaporated. Other concentrations studied were diluted from the stock *Citrus aurantium* fruit peels solution and the electrolyte medium was ensured with 1.0 M HCl solution.

2.3 Electrochemical analyses

The chemical composition (wt%) of mild steel electrodes in corrosion experiments is as follows: 0.08400 C, 0.21700 Cu, 0.01100 P, 0.10200 Si, 0.06030 Cr, 0.07890 Ni, 0.00222 Nb, 0.01100 V, 0.01040 Mo, 0.01900 S, 0.00198 Co, 0.40900 Mn, 0.01620 Sn, and the remain of Fe. Three electrochemical experiments were conducted using CHI-660B model electrochemical analyser with the known three electrode technique at 298 K. Mild steel was utilized as working electrode and it was applied with its cross-sectional area of 0.5024 cm². The surface of the working electrode was mechanically sanded by abrasive papers with 150 up to 1000 grid to provide the same surface roughness, then washed with purified water, and removed the grease with acetone. A platinum sheet with a surface area of 1 cm² was used as the counter electrode and Ag/AgCl electrode as the reference. The mild steel electrodes were immersed in the extract solutions for one-hour prior to beginning the electrochemical measurements in order to balance the system. EIS experiments were performed at 1x10⁵ to 5x10⁻³ Hz frequency ranges by applying amplitude of 5 mV to the process of corrosion inhibition. LPR experiments were carried out at ±10 mV (Ag/AgCl) ranges from the potential of corrosion (E_{corr}) with 0.1 mV s⁻¹ scan rate. The resistances of

linear polarization (R_p) were defined from the slope by plotting a potential versus current curve. The curves of potentiodynamic polarization were firstly constituted by utilizing -0.350 V from the E_{corr} to the cathodic potentials, after then $+0.350$ V from the E_{corr} to the anodic ones, with 1.0 mV s^{-1} scanning rate. The values of corrosion current density (i_{corr}) of the process were defined by Tafel extrapolation method from the potentiodynamic polarization plots.

Surface analyses of mild steel electrodes were viewed one hour of duration in the aggressive media with and without *Citrus aurantium* fruit peels extract by utilizing an OLYMPUS BX-51 (Centre Valley, PA, USA) model optical microscope with an integrated digital camera.

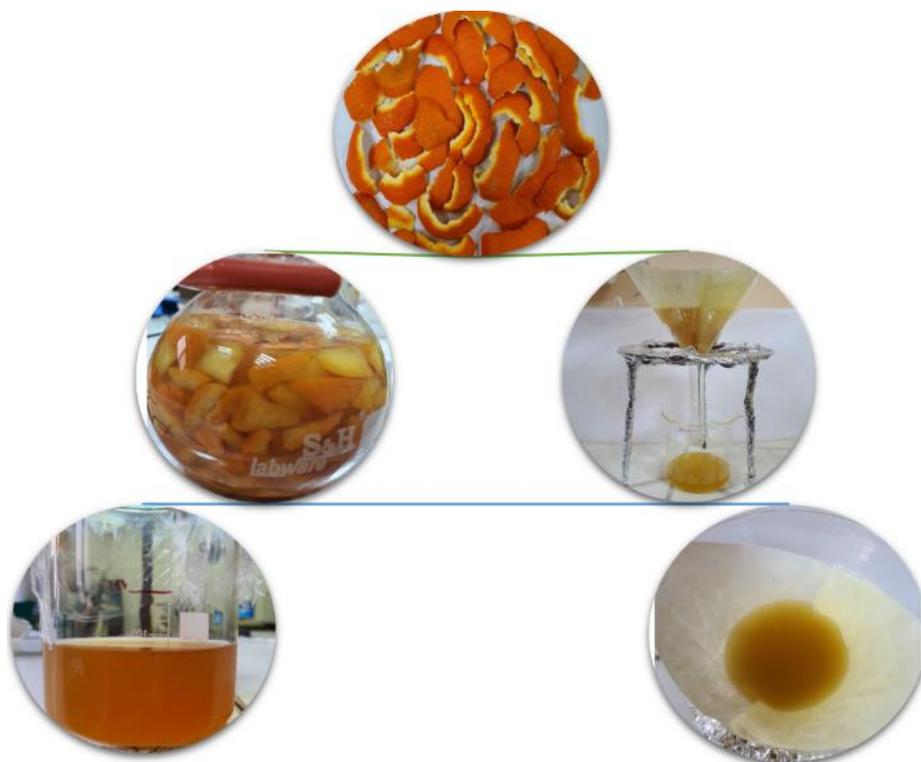


Figure 1. Stages of the extraction process

3 RESULTS AND DISCUSSION

3.1 EIS, LPR and potentiodynamic polarization experiments

Electrochemical impedance is a technique usually relied on implementing an alternative current potential to an electrochemical cell and surveying the current through that cell [12]. It is also one of the methods applied to get reliable information about the generally adsorption of inhibitors at the metal/solution interface [13]. The inhibitor effect of *Citrus aurantium* fruit peels extract at different concentrations on mild steel surface was examined by using EIS, LPR and potentiodynamic polarization techniques for 1-hour immersion time at 298 K. Two types of electrical equivalent circuit models in Figure 2 for inhibited and uninhibited 1.0 M HCl solutions were applied in this process.

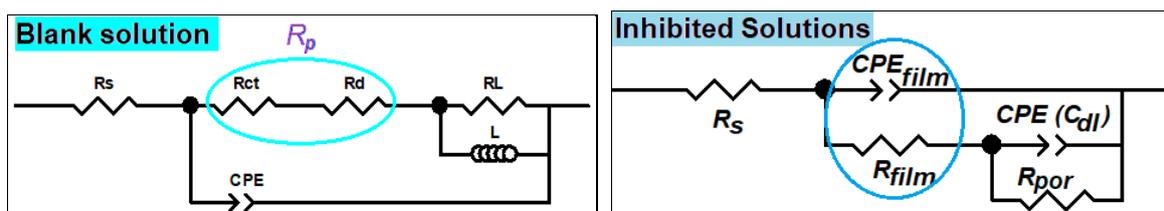


Figure 2. The two electrical equivalent circuit models proposed for blank and the inhibited solutions of the corrosion process (R_s : Solution resistance, R_d : Diffuse layer resistance, R_{ct} : Charge transfer resistance, L : Inductance, CPE : Constant phase element, R_L : Inductive resistance, R_{film} : Film resistance, CPE_{film} : Film capacitance, R_{por} : Pore resistance and $CPE(C_{dl})$: Double layer capacitance)

It will be clearly seen in Fig. 2 that the two circuits proposed are different from each other. The most apparent distinction for solutions containing the *Citrus aurantium* fruit peels extract is the inhibitor film composed on the metallic surface and the resistance it composes. The EIS (Nyquist) diagrams by fitting the experimental results in the ZView2 software program for one-hour immersion in the aggressive solution are given in Figure 3. The Nyquist plot consists of a depressed semicircle in the uninhibited (blank) solution. This indicates that the corrosion process of metal (mild steel) in 1.0 M HCl is generally charge transfer controlled [14, 15].

As can be understood more clearly from the Fig. 3, it can be said that as *Citrus aurantium* fruit peels extract is added in different concentrations to the 1.0 M HCl solution, the corrosion of mild steel electrodes decreases. *Citrus aurantium* adsorbed on the metallic surface actually prevents the corrosion by occurring a preservative film layer. On the other hand, it is clearly revealed that the diameters of the capacitive loops occurred accordingly increased with the rise in *Citrus aurantium* fruit peels extract concentration from the Nyquist diagram in Figure 3. EIS curves are defined in two ways as high and low frequency regions. In a corrosion process, the high frequency region is for the diffuse layer (R_d) and the charge transfer (R_{ct}). The low frequency one is the region where the inhibition takes place and is responsible for the film resistance (R_f) that accumulates on the mild steel surface and originates from *Citrus aurantium* fruit peels extract. It has been compatible with other research in literature [16-18]. Two constant phase elements (CPE) are also present for the inhibited extract solution process. First is the double layer capacitance (CPE_{dl}) and the second is film composed on the mild steel (CPE_{film}) which originates from the capacitance of film layer.

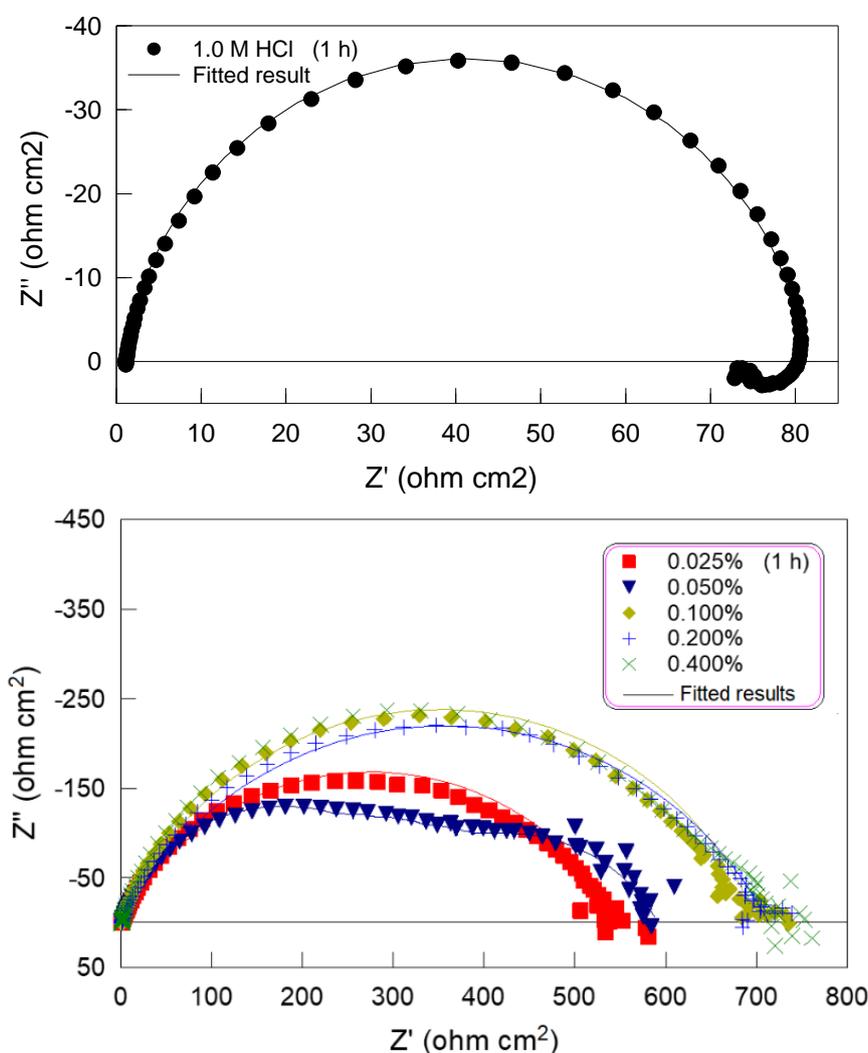


Figure 3. The Nyquist diagrams for 1 hour in 1.0 M HCl solutions with and without *Citrus aurantium* fruit peels extract at different concentrations

Corrosion inhibition data obtained by three applied electrochemical methods (EIS, LPR and potentiodynamic polarization) are presented in Table 1.

Table 1. EIS, LPR and Tafel extrapolation methods data of mild steel in HCl solution without and with *Citrus aurantium* fruit peels extract in different concentrations for one-hour immersion

C (w/v %)	EIS							
	E_{corr} (V/Ag/AgCl)	R_s (Ω cm ²)	CPE (μ F cm ²)		R_L (Ω cm ²)	L (H)	R_p (Ω cm ²)	η (%)
<i>Citrus aurantium</i>				n				
Blank	-0.474	1.2	110	0.94	8	4	72	-
0.025	-0.525	1.1	102	0.70	-	-	549	86.9
0.050	-0.517	1.2	92	0.70	-	-	590	87.8
0.100	-0.524	1.3	89	0.76	-	-	700	89.7
0.200	-0.530	1.2	75	0.76	-	-	712	90.0
0.400	-0.525	1.2	65	0.70	-	-	730	90.1
	*LPR							
<i>Citrus aurantium</i>	E_{corr} (V/Ag/AgCl)			R_p (Ω cm ²)			η (%)	
Blank	-0.475			71			-	
0.025	-0.532			573			87.6	
0.050	-0.521			612			88.4	
0.100	-0.531			676			89.5	
0.200	-0.529			717			90.1	
0.400	-0.528			726			90.2	
	**Potentiodynamic polarization							
<i>Citrus aurantium</i>	E_{corr} (V/Ag/AgCl)		$-\beta_c$ (mV dec ⁻¹)		i_{corr} (μ A cm ⁻²)		η (%)	
Blank	-0.475		108		265		-	
0.025	-0.533		101		35		86.8	
0.050	-0.523		99		31		88.3	
0.100	-0.531		100		30		88.7	
0.200	-0.532		102		29		89.1	
0.400	-0.530		100		28		89.4	

According to the EIS and LPR data, the E_{corr} values shifted to more cathodic potentials with rising *Citrus aurantium* fruit peels extract concentration compared to the blank solution. It is noticed in Table 1 that the CPE values obtained from the EIS experiments decrease with the increase of extract concentration. On the other hand, the “ n ” values, which are the surface roughness coefficient, were smaller in the solutions containing the *Citrus aurantium* fruit peels extract than the ones without. The R_p and R_p^* values in the EIS and *LPR measurements increase as the *Citrus aurantium* fruit peels extract is added to the blank solution (Table 1). This is due to the increase in the number of inhibitor molecules attached to the mild steel surface. The inhibition efficiency ($\eta\%$ and $\eta^*\%$) value of bitter orange extract after 1 h immersion at 0.400% (w/v) concentration was calculated as 90.1% and 90.2% by EIS and LPR techniques, respectively. And it can be said that bitter orange extract exhibits extremely effective protection against corrosion of mild steel in the 1.0 M HCl solution.

The relevant parameters for the dissolution process of mild steel are given in **Table 1, calculated from the linear region of the cathodic potentiodynamic polarization curves by means of the Tafel extrapolation method. Potentiodynamic polarization curves of mild steel in 1.0 M HCl for various *Citrus aurantium* fruit peels extract concentrations at 298 K are revealed in Figure 4.

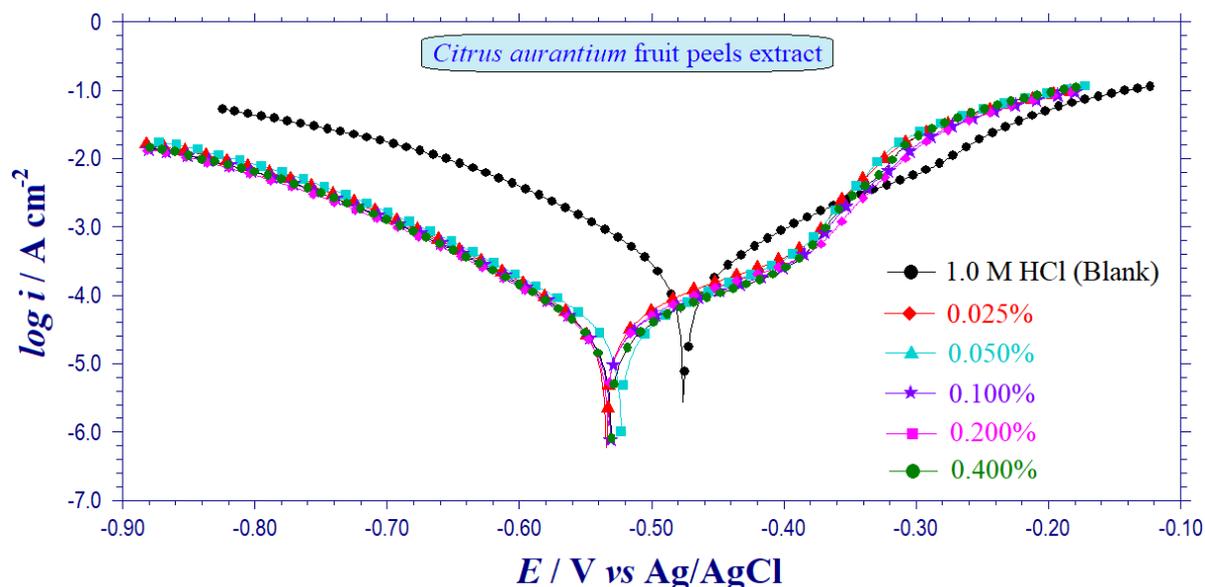


Figure 4. Potentiodynamic polarization plots of mild steel in HCl solution for different concentrations of *Citrus aurantium* fruit peels extract at 298 K

It can be plainly seen from Table 1 that the values of corrosion current density (i_{corr}) of *Citrus aurantium* fruit peels extract were smaller than those of the blank solution. It means that it inhibits anodic dissolution of mild steel. The i_{corr} values attenuate from $265 \mu\text{A cm}^{-2}$ to $28 \mu\text{A cm}^{-2}$ with rising concentration and the highest inhibition efficiency was 89.4% in the 0.400% (w/v) *Citrus aurantium* fruit peels extract solution.

This result was also very compatible with the values calculated by the other two electrochemical techniques. According to Table 1, it was seen that $-\beta_c$ values did not change much, and as a result, it was concluded that the hydrogen evolution mechanism was not affected much by the presence of *Citrus aurantium* fruit peels extract. The E_{corr} values in the potentiodynamic polarization plots alter considerably to the more cathodic (negative) potential with rising concentration of the *Citrus aurantium* fruit peels extract, just like in the other two electrochemical methods. This potential alteration is within the limit of the potential scale used by Antropov [19]. Figure 4 shows that there is a remarkable current reduction on the side of the cathodic polarization plots compared to that of the blank solution. As a result of this, *Citrus aurantium* fruit peels extract can be defined as a cathodic type inhibitor for mild steel in 1.0 M HCl solution [20, 21]. It can be said that the *Citrus aurantium* fruit peels extract is strongly adsorbed on the metal surface according to the inhibition efficiencies values obtained by all three-experimental measurement techniques.

3.2 The optical surface microscope images of mild steels

The effect of protective *Citrus aurantium* fruit peels extract as green corrosion inhibitor adsorbed on mild steel electrode in 1.0 M HCl after one-hour immersion was analysed by using optical microscope technique as indicated in Figure 5. Surface images were carried out for 0.400% (w/v) C. aurantium fruit peels extract solutions without and with 1.0 M HCl. In this study, the experimental data provided by electrochemical experiments are approved by surface morphologies viewed with an optical microscopy. The optical microscope images clearly reveal that the surface in the uninhibited medium are strongly damaged. The inhibited surface is virtually free from pits and it is smoother than the uninhibited one. As a result, it can be said that there is clear evidence that C. aurantium fruit peels extract is adsorbed on the mild steel surface.

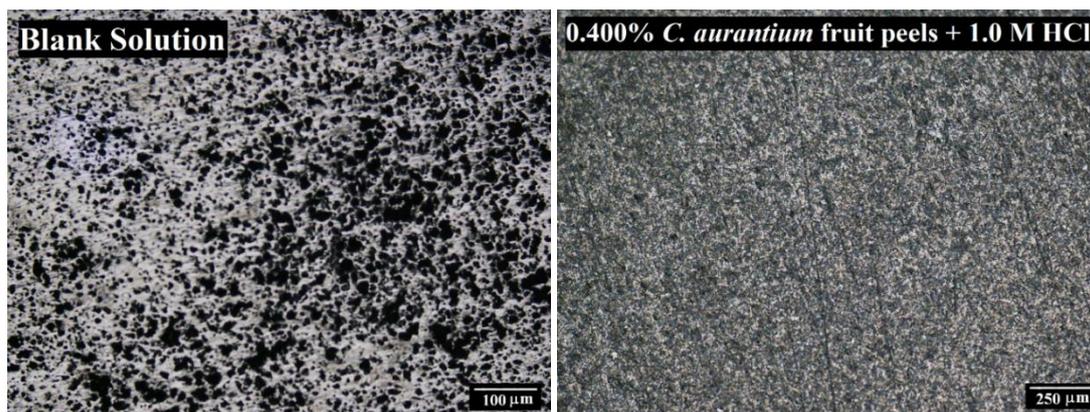


Figure 5. Optical microscope morphologies of the mild steel electrodes for one hour at 298 K

After the surface morphologies, there is a marked interaction between the applied green inhibitor and the metal, and it supports all three experimentally investigated electrochemical techniques.

4 CONCLUSIONS

In this study, the effect of *C. aurantium* fruit peels extract as a green inhibitor, which is environmentally-friendly and rich in vitamin C, was analysed by all three electrochemical experiments on the corrosion behaviour of mild steel in HCl medium. It was followed that the *Citrus aurantium* fruit peels extract was highly adsorbed on the metallic surface and shown great inhibition even at all concentrations of extract. The inhibition efficiencies increased due to the increase in the concentration of *C. aurantium* fruit peels extract with all three experimental methods. EIS results showed that the R_p values raised and the CPE values attenuated with the rise in the concentration of the bitter orange extract, that is, the metal surface protection effect of the extract increased. According to this result, it can be stated that the increment in the extract concentration, whose inhibitory effect was investigated, is related to the rising in the number of organic components adsorbed to the metallic surface.

According to the results acquired from the potentiodynamic polarization plots, the calculated cathodic Tafel constant values did not alter much around 100 mV dec^{-1} in 1.0 M hydrochloride solutions without and with *Citrus aurantium* fruit peels extract, indicating that the mechanism of hydrogen evolution was not influenced by the extract. The *C. aurantium* fruit peels extract acts as a cathodic inhibitor, since it affects the corrosion of mild steel in solution, by significantly reducing the cathodic currents at every concentration.

In order to better examine the influence of the *C. aurantium* fruit peels extract on the mild steel, it was monitored that the surface morphology in the extract solution was pretty smooth and the cavities were closed clearly compared to the morphology in the blank solution. The three experimental methods applied and the optical microscope images findings are quite compatible with each other. The chemical structures of phytochemicals (secondary metabolites) found in bitter orange fruit peels are rich in both aromatic ring and π -electrons, and heteroatoms. Therefore, in this respect, these properties are among the main reasons for their high inhibition efficiency in preventing metal corrosion.

Author Contributions

Demet ÖZKIR: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition

All authors read and approved the final manuscript.

Conflict of interest

No conflict of interest was declared by the authors.

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