Materials Research Express

PAPER

Adsorption ability, stability and corrosion inhibition mechanism of phoenix dactylifera extract on mild steel

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Keywords: adsorption, natural wastes, date palm (Phoenix dactylifera), seed extract, mild steel corrosion, phase angle.

Abstract

Adsorption ability, stability and corrosion inhibition of phoenix dactylifera (date palm) seed extract (PDSE) as a natural corrosion inhibitor were studied on mild steel (MS) in 1 M HCl solution after different exposure times. Linear polarization resistance (LPR), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) techniques were utilized to define the inhibiting performance of the extract on the rate of corrosion. The stability of the organic film formed over the metal surface was investigated with the help of chronoamperometry (CA) technique. The MS surface was characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD) and contact angle measurements. Surface charge of the metal after exposing to the solution was determined by measuring the potential of zero charge (PZC) using the EIS technique and an adsorption mechanism was proposed. The results of the electrochemical measurements showed that PDSE reduces sufficiently the rate of MS corrosion. The SEM studies showed that the inhibitor strictly attached to the metal surface and form a protective film over the metal surface. The average inhibition efficiency determined from LPR, EIS and PP techniques was found to be 97.3%, which is quite efficient for the practical applications.

1. Introduction

Corrosion is one of the most serious problems in the iron and steel industries [1, 2]. Acid solutions such as HCl and H2SO4, which are commonly used in the steel pickling, cause corrosion of metals [3, 4]. Unfortunately, there is no method to completely eliminate the corrosion process. On the other hand, many approaches have been made to slow down the rate of corrosion. Among them, the most practical and common method is the use of inhibitors to protect metals against corrosion [5–10]. When inhibitors are added to corrosive media in small amounts, the corrosion rate of metals may significantly reduces. Organic compounds are generally preferred for this aim. The organic compounds bearing active adsorption centres such as oxygen, nitrogen or sulphur atoms as well as, containing n electrons in conjugated double bonds or triple bonds are reported to be effective for protecting metals [11–13]. However, most of organic inhibitors suggested for this aim have some disadvantages, such as low efficiency, high cost and hazardous effects on human or environment, which restrict their practical usage. In order to overcome these drawbacks, it is needed to find new and applicable corrosion inhibitors. In this sense, researchers have focused on eco-friendly, and renewable natural waste resources to be used for protecting metals against corrosion. Plant-based natural wastes contain many functional organic compounds including tannins, organic acids, alkaloids, saponins, terpenoids and flavonoids, and are called green inhibitors [14]. Green inhibitors, which do not contain heavy metals or toxic compounds, have been reported as corrosion inhibitors for different metals in acidic solution [15–19]. The reported studies indicated that the tested inhibitors could slow down the corrosion rate of metals in alkaline or acidic environments.
Corrosion inhibition effect of aqueous seed extract of *Phoenix dactylifera* against MS corrosion was reported in 2 M H$_2$SO$_4$ solution using mass loss and hydrogen evolution techniques [20]. It was found that the inhibition effect of the inhibitor changes with the inhibitor concentration, immersion time and temperature. Yamuna and Anthony [21] reported the inhibition effect of *Citrus medica* leaf for corrosion of carbon steel using electrochemical methods. The researchers showed that *Citrus medica* leaf has a good inhibition performance (81.75%) at 300 ppm. Inhibition performance of the extracts increases with increasing the extract concentration. In another study, fenugreek leaves and lemon peel as a green corrosion inhibitor for mild steel was studied in 1 M acidic solutions was studied by weight loss and electrochemical methods. The authors obtained plant extracts from an acidic solution. In addition to these studies, many researchers have investigated the inhibitory activity of bark, stem and leaf isolates of various plants as green inhibitors. Also, the corrosion inhibition effects of extracts of ginger [25], *Prunus dulcis* peels [26], the extract of olive leaves [27], palm oil from seed [28], pomegranate peel [28] have been reported in the literature. A comparative data with this study are summarized in tables 1 and 2.

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2. Experimental

2.1. Preparation of inhibitor and test solution

The natural compound used for MS protection were obtained from a local market in Bingöl, Turkey. The samples were dried on unprinted papers in a sun-free environment. At the end of the drying process, the seeds were milled in a laboratory mill and passed through a 30 mesh analysis sieve. The powdered seeds (100 g) were put into the maceration container. 2 L of methanol: dichloromethane solvent system (1:1; v-v) was added each time. The mixture was stirred in an orbital shaker for 48 hours under laboratory conditions. This process continued until the transition of organic matter was completed. A total of 6 L of solvent was used for maceration.

Then, the isolate was filtered through Whatman no:1 filter paper. The resulting isolate solutions were combined and the solvent was removed by rotary evaporation under reduced pressure at 40 °C to give dry PDSE. The obtained isolate was taken into an amber glass bottle and stored in a refrigerator (+4 °C) for further analysis and measurements.

All corrosion tests were carried out in 1 M HCl solution without and with the addition of the extract. The temperature of the test solutions was kept at 298 K during the electrochemical measurements.

2.2. Preparation of electrodes

MS working electrodes were prepared as specified in reference [4]. Their chemical composition was (wt%) C (1.720), O (0.115), Al (0.173), Si (0.133), P (0.052), Cu (0.144), Cr (0.057), Mn (0.704), Sn (0.126), Mo (0.204), Ni (0.115), and Fe (remainder). The exposed surface area of the MS electrodes was 0.785 cm². The surface of MS electrode, which was exposed to the test solution was polished with different emery papers, which ended with 1200 grit before the experiments. Then, the electrodes were washed with distilled water, degreased with ethanol, washed with distilled water once again and finally dried with napkin paper. After cleaning electrode surface, the electrode was exposed to the test solutions as soon as possible. A platinum sheet (Pt) with 2 cm² total surface area and a commercially purchased Ag/AgCl (3.0 M KCl) were used as counter and the reference electrodes, respectively for all electrochemical experiments.

2.3. Electrochemical measurements

A CHI6096E Electrochemical Workstation was used for all electrochemical experiments. Prior to each measurement, the electrodes were immersed in a corrosive test solution for 6 h. Polarization curves were obtained with a scan rate of 1 mV s⁻¹ in the potential range from −0.6 V to −0.2 V (Ag/AgCl). EIS measurements were performed at open circuit potentials (Eocp) between 100 kHz and 0.01 Hz by applying 5 mV amplitude. LPR measurements were carried out by recording the electrode potential ± 10 mV around Eocp with 1 mV s⁻¹ scan rate.

The stability of the inhibitor film assembled on the steel surface was examined with the help of CA. The CA measurements were made by applying constant anodic or cathodic overpotentials for 1 h and 6 h in the absence and presence of the inhibitor. The PZC of MS was determined in 1 M HCl solution in the presence of 2000 ppm PDSE with the help of EIS measurements after 6 h immersion.

2.4. Surface characterization measurements

The surfaces of the steel samples after exposing to 1 M HCl solution in the absence and presence of 2000 ppm PDSE for 1 h and 6 h were examined by SEM (Joel 6510). The hydrophobic/hydrophilic properties of MS, which was exposed to 1 M HCl solution without and with the addition of 2000 ppm PDSE, were investigated by contact angle measurements, which were performed using sessile water drop method using a contact angle measuring system XRD studies. The MS was immersed in 1 M HCl solutions with 2000 ppm of PDSE extract for 1 h and 6 h. The product formed over the steel surface was analysed by XRD.

3. Results and discussion

3.1. Potentiodynamic polarization measurements

The MS specimen was treated to 1 M HCl solution containing 2000 ppm PDSE and PDSE-free solution at room temperature for 6 h and PP measurements were obtained. The curves obtained are presented in figure 1. Some electrochemical parameters such as corrosion potential (Ec,corr), corrosion current density (i,c,corr), corrosion rate (W) and percentage inhibition efficiency (η%) values were calculated from these curves and the data calculated are listed in table 1.

         i,c,corr values were calculated by extrapolating the linear part (Tafel region) of the curves to their corresponding E,c,corr. The W was calculated from to the following equation (1) [4];
In this equation, \( t \) is exposure time, \( M \) is the molar weight of iron and \( F \) is Faraday constant. The \( \eta \% \) values were determined using the equation given below \([33]\);

\[
\eta \% = \left( \frac{i' - i}{i} \right) \times 100
\]

where \( i' \) and \( i \) are corrosion current densities of MS in the uninhibited and inhibited acid solutions, respectively.

As it is seen from figure 1, both anodic and cathodic semi-logarithmic polarization curves of MS electrode are almost parallel. This behaviour suggests that the corrosion mechanism of the steel does not change with the addition of the inhibitor to the aggressive solution. As it is clearly seen from from figure 1 and table 1, the addition of PDSE to HCl solution shifts \( E_{\text{corr}} \) towards more negative potential with respect to inhibitor-free solution (from \(-0.486 \text{ V} \) to \(-0.505 \text{ V} \) versus Ag/AgCl). Therefore, PDSE could be classified as mixed-type corrosion inhibitor with predominant control of the cathodic reaction \([34, 35]\).

Both anodic and cathodic current densities also reduce after the addition of inhibitor to the corrosive solution; \( i_{\text{corr}} \) slowers significantly, which is dependent on the inhibitor concentration. The reduction in \( i_{\text{corr}} \) after the addition of the inhibitor may be arises from the formation of a protective inhibitor layer assembled on the metal surface.

According to data presented in table 1, \( W \) and related \( i_{\text{corr}} \) values decrease more and more when PDSE is added to 1 M HCl solution. The inhibition efficiency at 2000 ppm PDSE is 98.80%. Pramudita and co-workers \([29]\) found that *Terminalia catappa* leaves decreases corrosion rate of MS in 1 M H2SO4 within 6 hours immersion period. However, the corrosion rate of the steel in the case of this extract is high with respect to PDSE. The similar data were obtained for some other natural products, which are summarized in tables 1 and 2. The comparative data provided in these tables indicates that the inhibitory performance of PDSE is good \([30–32]\).

### 3.2. Electrochemical impedance spectroscopy measurements

In the EIS measurements, we determined the corrosion protection ability of PDSE (2000 ppm) in 1 M HCl solution after 6 h immersion. Nyquist and Bode plots of the steel electrode are shown in figure 2. As it can be seen from figure 2(a) the Nyquist plot of MS electrode in 1 M HCl solution consisted of a single depressed capacitive semi-circle shape and only one time-constant is appeared at the Bode plots (figure 2(b) and (c)). The addition of the inhibitor to the corrosive solution does not affect appearance of the plots. These observations demonstrate that the corrosion mechanism does not change with the addition of the extract to the acid solution. The depressed semicircle from ideal appearance is generally explained by inhomogeneities of the electrode surface, impurities and distributions of active sites on the solid surface \([35, 29–32, 36]\). These observations indicate that the corrosion process of MS in 1 M HCl solution in the absence and presence of PDSE is activation-controlled.

MS/solution interface is modelled with the electrical equivalent circuit diagram proposed in figure 2(a) as inset. In this model, polarization resistance \( (R_p) \) and constant phase element \( (CPE) \) are connected in parallel with each other and solution resistance \( (R_s) \) in series with both. Some electrochemical parameters, such as \( R_p \), \( CPE \) and \( n \) (degree of surface inhomogeneity) values were determined from fitting experimental data to this model via the ZView software programme and given on table 2. The \( \eta \) values of the inhibitor were calculated from EIS data according to the following formula:
where $R'_p$ and $R_p$ are the polarization resistances of MS obtained in the uninhibited and inhibited acid solutions, respectively [37].

Data are given in figure 2 and table 2 clearly indicate that when the inhibitor was added to aggressive solution, the values of $R_p$ increases most probably adsorption of more inhibitor molecules over the steel surface or increasing quality/thickening film since more PDSE molecules presence in the solution [37]. The resulting inhibitor film is acting as a barrier between the metal and the corrosive solution, which prevent the metal against corrosion.

The interface of MS/solution does not behave as an ideal capacitor because of the roughness or unstable current distributions on the electrode surface. The data presented in table 2 indicate that $CPE$ values decrease

$$\eta\% = \frac{R'_{p} - R_p}{R'_{p}} \times 100$$ (3)
with addition of the inhibitor in the corrosive solution. This is due to a decrease in dielectric constant or an increase in electrical double layer thickness. This type of behaviour is observed in systems where inhibition occurs due to the adsorption of the inhibitor molecules on metal surfaces by forming a protective surface film [37] 95.7% inhibition efficiency was achieved when 2000 ppm PDSE is added to 1 M HCl solution for 6 h.

3.3. Linear polarization measurements
The LPR is a suitable electrochemical technique to determine resistance appeared at the metal/solution interface at limited potential range around open circuit potential. The $R_p$ of MS in 1.0 M HCl solution with and without 2000 ppm of PDSE was also studied by LPR technique. From the current-potential curves, $R_p$ was calculated and provided on table. The $\eta$ was calculated from equation (3) and given on the same table. As it is seen from table 2, EIS and LPR results are very comparable; the addition of PDSE inhibits corrosion of the steel which is enhanced more and more with the increase compared to inhibitor free solution.

Electrochemical data clearly indicate that the isolate obtained from the special organic solvent mixture applied in this study performs better corrosion protection ability with respect to the isolates obtained from distilled water [38] and acidic aqueous solutions [39].

3.4. Chronoamperimetry measurements
In order to determine the stability of the assembled film over the metal surface CA measurements were performed. For this aim 100 mV anodic or cathodic overpotentials ($E_{corr} \pm 100$ mV) were applied to the system for 3600 s and the current densities observed were plotted against operation time (figure 3). As a reference points, the similar measurements were also performed for a blank solution and the data obtained are comparatively given on figure 3. The data presented in figure 3 show that anodic current density in the absence of the inhibitor increases sharply during the initial of the operation, which can be assigned to access dissolution of the steel and thus increases real surface area [40, 41]. But, the cathodic current density is almost constant during the electrolysis. However, when PDSE is added to the aggressive solution, both anodic and cathodic current densities decrease significantly. Increasing anodic current density during the initial of the electrolysis may result from partly removing inhibitor film or its destroying. The results presented here indicate that the inhibitor film formed over the steel surface is electrochemically stable in acidic media, which is an advantage for the practical applications.

3.5. Surface characterization measurements
Figure 4 shows the surface contact angles for MS electrode in 1 M HCl solution without and with the addition of 2000 ppm PDSE after exposing the MS to the test solutions for 6 h. The contact angle was determined as 18.0° in 1 M HCl solution. The addition of 2000 ppm PDSE increases contact angle from 18.0° to 45.26°. Therefore, it can be said that the hydrophobic character of the surface increases due to the adsorption of organic molecules over the surface [42–44].

The surface structures of the MS specimens after exposing to the test solutions for 6 h were examined with SEM measurements and the images obtained are shown in figure 5. As it is clearly seen from figure 5, the surface of MS electrode is strongly damaged in 1 M HCl solution most probably due to the excessive dissolution of steel; many cracks and pits distributed over the steel have appeared. However, after the addition of 2000 ppm PDSE to the corrosive solution, the MS surface looks much better. A very homogenous and adherent inhibitor film appears on the steel surface, which reduces the dissolution of the steel in corrosive media and provides significant prevention against corrosion. The data obtained here support the results of electrochemical measurements and suggest that this extract is a good corrosion inhibitor for mild steel protection in HCl solution.

3.6. X-ray diffraction study
The surface of MS after exposing to corrosive solution in the presence of 2000 ppm plant extracts for 1 h and 6 h were examined with XRD. For comparison the XRD patterns of MS were also given in the same figure (figure 6). The comparison between the diffraction diagrams given on figure 6 clearly shows that there are not significant differences between the XRD pattern of un-corroded and corroded surfaces after exposing to 1.0 M HCl + 2000 ppm PDSE for 1 and 6 h. The strong peak intensity observed around 45° at 2θ are related to Fe phase and the peaks related to iron oxides are not observed. Therefore, we could that the inhibitor prevent MS dissolution significantly. The reduction in the peak intensity is indicative of the bonding between MS and molecules of inhibitor contained in PDSE, possibly due to metal complex formation [45].

3.7. The potential of zero charge and the inhibition mechanism
Adsorption of organic species over the metal surfaces occurs by the adsorption of inhibitor molecules through the displacement of initially adsorbed water molecules on the metal surface as given below [46],
In order to determine the excess surface charge of the metal, the potential of zero charge (PZC) determination studies were made after exposing the metal to the corrosive media for 6 h in the acidic media with or without inhibitor. A plot of $R_p$ versus applied potential was obtained and is shown on figure 7. The potential obtained at maximum point of the plot, $R_p = -0.488$ V is called as $E_{pzc}$. On the other hand, the $E_{ocp}$ in the same conditions is $-0.507$ V for inhibitor-free 1 M HCl solution. The $E_r$, Antropov’s ‘rational’ potential of corrosion calculated from $E_r = E_{ocp} - E_{pzc}$, $E_r$ was found to be -0.019 V, which indicates excess negative charge on the MS surface.

\[
\text{Inh (solution) + } n\text{H}_2\text{O}_{\text{adsorption}} \leftrightarrow \text{Inh}_{\text{adsorption}} + n\text{H}_2\text{O}_{\text{solution}}
\]  

(4)

Figure 3. Chronoamperometry curves of MS obtained in 1 M HCl solution in the absence (○) and presence of 2000 ppm PDSE (●) after 1 h (a) and 6 h (b) immersion.

Figure 4. Contact angles measured over MS surface in the absence (a) and presence of 2000 ppm PDSE (b) after 6 h immersion.
The PZC value was determined as $-0.532$ V in inhibitor containing medium and the $E_{ocp}$ value is $-0.512$ V. In this case, the $E_r$ was calculated as $+0.020$ V, which shows that the surface of the metal in this conditions has excess positive charge [47, 48].

When the metal surface posses positively charged in the corrosive media, negative species such as chlorine ions are adsorbed on the surface of the metal initially and attracts cationic forms and protonated water molecules. So close-packed triple-layer will form on the metal surface and inhibit MS dissolution [49–51].

4. Conclusions

In this study, adsorption ability, stability and corrosion inhibition of PDSE on MS was studied in 1 M HCl solution using various electrochemical techniques. According to the data obtained, following important points can be summarized:
1. PDSE acts as a good corrosion inhibitor with high inhibition efficiency (more than 95%) in acidic solution after 6 h immersion.

2. The isolate obtained from an organic solvent mixture (applied in this study) performs better corrosion protection ability with respect to the isolates obtained from distilled water and acidic aqueous solutions reported in literature.

3. PP studies shown that PDSE reduces both anodic dissolution of metal and also the rate of cathodic hydrogen evolution reactions.

4. PDSE behaves as mixed-type corrosion inhibitor with predominant cathodic effectiveness.

5. The CA results indicated that the film assembled over the MS surface is stable.

6. PZC results showed that, the excess surface charge of the metal in the presence of inhibitor was positive.

7. The surface hydrophobicity increases by adding the PDSE to the aggressive solution.

8. The SEM and XRD studies showed that the surface inhibitor film reduces the corrosion rate of MS in HCl solution.

Acknowledgments

This study has been financially supported by the Bingöl University Scientific Research Projects (BÜBAP, Project Number: GMYO.2018.00.002) Coordination Unit. The authors are greatly thankful to BÜBAP, Health Sciences Faculty, Occupational Health and Safety Department and Bingöl University Central Laboratory.

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Figure 7. PZC curves of MS in 1 M HCl solutions in the absence (a) and presence (b) of 2000 ppm PDSE after 6 h immersion.
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