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Short Communication

Davidian involucrata Leaves Extract as Green Corrosion Inhibitor for low carbon Steel in concrete pore solution containing chloride ions

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In this work, we tried to use the Davidia involucrata leaves extract (DILE) as an eco-friendly inhibitor to enhance corrosion resistance of carbon steel plate in concrete pore solution containing chloride ions. The inhibiting performances of DILE were studied by electrochemical impedance spectroscopy and polarization analysis. Electrochemical results indicated that the DILE was an effective corrosion inhibitor in decreasing the corrosion behavior of carbon steel at the optimal dosage of 100 mg/L inhibitor. The potentiodynamic polarization results indicate that the DILE was a blended-type inhibitor that enhanced the performance of corrosion resistant in carbon steel plate considerably with formation of an organic layer to restrain both the anodic and the cathodic reactions. The surface morphology of a carbon steel plate immersed in concrete pore solution containing 100 mg/L DILE inhibitor revealed the formation of low corrosion products on steel which was in agreement with the results achieved from electrochemical assessments.

Keywords: Green inhibitor; Electrochemical corrosion; Carbon steel plate; Electrochemical impedance spectroscopy; Concrete pore solution

1. INTRODUCTION

Carbon steels and its alloys are widely used in numerous industries such as aerospace, automotive and construction due to the excellent formability and high production rate [1]. Aggressive solutions such as acidic and saline environments are the most corrosive in nature for carbon steel alloys than the other corrosive environment [2-4]. Hence, it is required to consider the protection of corrosion steels in saline solutions. The corrosion resistance of carbon steel depends on the stability and the presence of oxide film on its surface [5].

Corrosion inhibitors are usually used in industries to decrease the corrosion rate of carbon steels [6]. However, most compounds are artificial chemicals that can be very expensive and dangerous for living organisms and the environment [7, 8]. Thus, to develop environmentally friendly and most effective corrosion inhibitors, the synthesis of green corrosion inhibitors is very attractive among researchers [9, 10]. Green inhibitors are available as essential oils or extracts. Different parts of plants have some compounds that meet these criteria, so plants are a potential source of novel corrosion inhibitors [11]. Numerous scientific studies were recently achieved to consider the effect of some natural substances as green inhibitors on the corrosion of various metals, such as steel, in different corrosive media [12].

However, many studies have been done to evaluate the green corrosion inhibitors for carbon steels [13-15], the Davidia involucrata leaves extract (DILE) has never been investigated as an inhibitor of carbon steel corrosion in concrete pore solution. Therefore, this study aimed to evaluate efficiency of a natural DILE as a corrosion inhibitor for carbon steel in concrete pore solution containing chloride ions. Electrochemical tests were used to consider the inhibition efficiency for 24 h exposure time. Furthermore, the influence of temperature and inhibitor concentration were investigated.

2. MATERIALS AND METHOD

In order to study the effect of green inhibitors on corrosion behavior of carbon steel, electrochemical tests were done on Q235 carbon steel plates with 2 mm thickness, 10 cm length and 5 cm width in concrete pore solution. The composition of the used steel is presented in Table 1.

Table 1. The composition of Q235 carbon steel plate (wt%)

C	Mn	P	Si	S	Fe
0.17	0.43	0.045	0.23	0.050	Residual

The steel plate was cleaned with silicon carbide sheet, and then dipped and washed by acetone and DI water.

The Davidia involucrate leaves (DIL) was washed by DI water and dried at room temperature. Then it was successfully powdered and 8 g of powdered DIL were mixed by 0.5 L DI water in a magnetic induction stirrer at 70 °C for one hours. Then, the obtained solution was filtered by a filter paper. After that the solution was stirred once more at 70 °C for one day. The gel was then obtained with high viscosity and powdered. Finally, the obtained powder was applied as a corrosion inhibitor in all experiments. The tests were performed in concrete pore solution containing a combination of 0.2 M NaOH, 0.5 M KOH and 0.3 M $Ca(OH)_2$ with 13 pH containing 3.5wt% $CaCl_2$ as a source of chloride ions with 0, 10, 50 and 100 mg/L of DILE at 15, 25 and 35 °C.

A three-electrode cell was used during the electrochemical tests, with Q235 carbon steel and saturated calomel and platinum electrodes as a working, reference, and counter electrodes, respectively. Electrochemical impedance spectroscopy (EIS) analysis was performed at the frequency wide-ranging between 0.1 MHz and 10 mHz at 10 mV applied AC amplitude. The potentiodynamic polarization characterizations were done at a scanning rate of 1 mV/s. The surface morphologies of the steel samples were conducted using scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

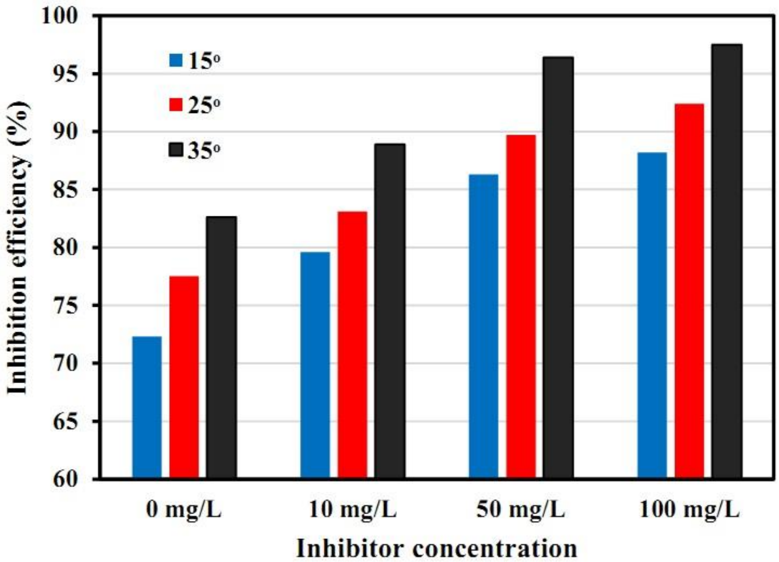

Figure 1. The temperature effect on inhibition efficiency of steel in different concentrations of DILE in concrete pore solution

The temperature value of the examination solutions with and without DILE inhibitor was done at the temperature of 15, 25 and 35°. Figure 1 indicates the temperature effect on inhibition efficiency of steel in different concentrations of DILE in concrete pore solution. As shown in Fig. 1, the inhibition efficiency increases when the concentration of DILE and temperature value increases. The 50 and 100 mg/L of DILE concentration presented highest inhibition efficiency of 94.69 and 94.81% at the temperature of 35°, respectively. At lower concentration, the DILE gave a significant inhibition efficiency of 90.5% at 35°. The DILE acts as a promising inhibitor in both higher temperature and concentration. Hot solution is commonly used for removing oxide scales from the surface of metal in many industries at high temperature in concrete pore solution. An enhancement in inhibition efficiency with increasing in temperature value is frequently interpreted as indicating the formation of chemical adsorption mechanism, although decreased inhibitory efficiency is attributed to the mechanism of physical absorption with increasing temperature [16]. The obtained results reveal that the adsorption of phytochemical compounds of the DILE on the surface of carbon steel is chemisorption.

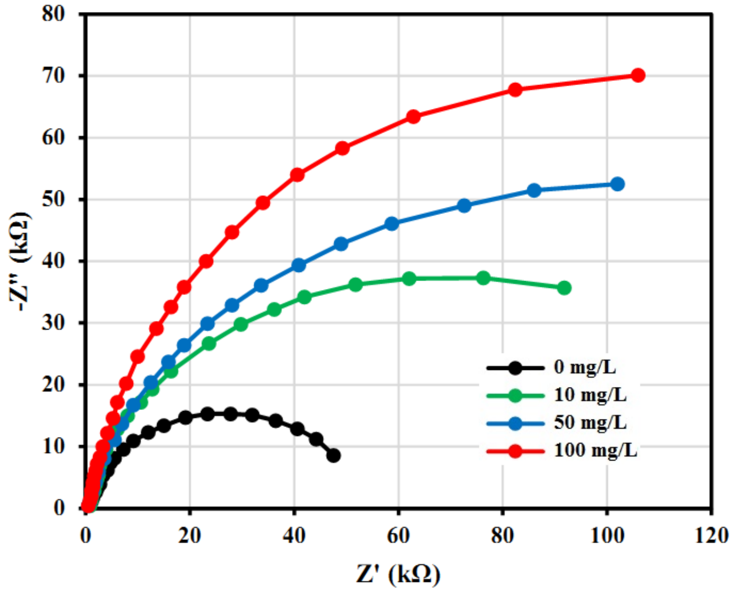

Figure 2. EIS diagrams of Q235 carbon steel into the concrete pore solution with various concentration of DILE inhibitor after immersion time of 18 h at temperature of 25°.

The Nyquist plots after immersion time of 18 h at temperature of 25° with different concentration of DILE inhibitor indicate in Figure 2.

As shown, when the carbon steel samples were exposed to concrete pore solution without DILE inhibitor, the Nyquist plot indicated a complete half semicircle loop. While the sample that was immersed into the solution with DILE revealed larger radius and an incomplete semicircle loops than the one without DILE inhibitor, showing a greater corrosion resistance behavior in solution with inhibitor. As the concentration of DILE inhibitor increased, the diameter of semi-circle loop increased due to the adsorption of DILE or formation of passive film in anodic site of Q235 carbon steel plate and thus reduced the dissolution of iron [17]. The passive layer reduced the attack of chloride ions toward the carbon steel surface and competently controlled the pitting corrosion.

Figure 3 revealed a used equivalent circuit model in this study. Where R_s is solution resistance. R_f and C_f indicate the resistance and the capacitance of passive film, respectively [18]. C_{dl} andR_{ct} are the double-layer capacitance and the charge transfer resistance of the carbon steel surface, respectively [19]. The obtained dataare shown in Table 2.

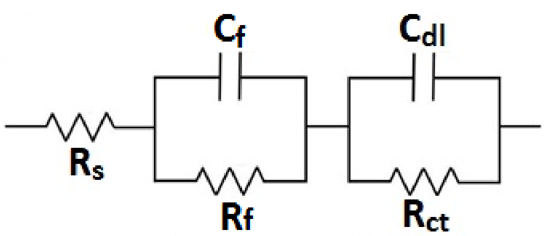

Figure 3. A fitted circuit model

As shown, the R_{ct} values were significantly increased from 53.2 kΩ to 289.4 kΩ, as content of DILE inhibitor increased in the concrete pore solution which indicated that the presence of DILE caused to improve the corrosion inhibition of Q235 steel.

Table 2. EIS parameters for Q235 steels into the concrete pore solution with various concentration of DILE inhibitor after immersion time of 18 h at temperature of 25°.

DILE contents	R_s (Ω cm^2)	R_f(kΩ cm^2)	C_f(μF cm^{-2})	R_{ct} (kΩ cm^2)	C_{dl}(μF cm^{-2})	IE (%)
0 mg/L	53.1	28.4	.63	54.6	9.3	0
10 mg/L	48.7	98.7	2.8	159.7	4.4	65.8
50 mg/L	49.8	131.2	2.1	188.3	3.6	71.0
100 mg/L	52.9	169.1	0.8	278.5	1.5	80.3

Inhibitor efficiency (IE) was measured with the following equation:

$$IE\ (\%) = 100\times(R_{ct} - R_{ct}^*)/\ R_{ct} \quad (1)$$

whereR_{ct} is charge-transfer resistance with DILE inhibitor and R_{ct}* is charge-transfer resistance without DILE inhibitor.

From Table 2, it was found that the values of C_{dl} reduced after the addition of DILE inhibitor in the concrete pore solution which can be attributed to the inhibitor adsorption on the carbon steel surface leading to form protective layer on carbon steel surface [20]. Thin layer acts as a barrier between corrosion medium and steel surface. The inhibitor indicates maximum inhibition efficiency of 80.3% in concrete pore solution.

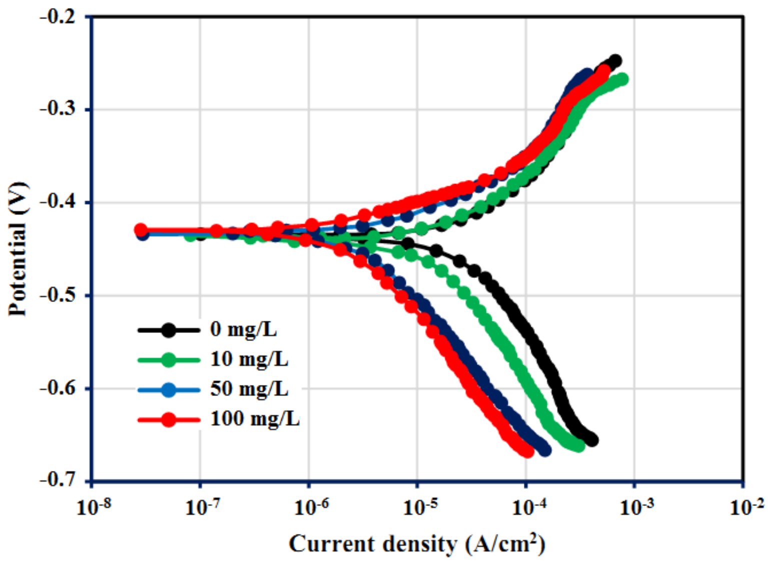

Figure 4. Polarization plots of carbon steel in electrolyte solution with and without DILE inhibitor after immersion time of 18 h at temperature of 25°

Figure 4 shows polarization diagrams of carbon steel in electrolyte solution with and without DILE inhibitor after immersion time of 18 h at temperature of 25°. Figure 4 reveals that both cathodic and anodic reactions of carbon steel corrosion are inhibited in the presence of DILE in concrete pore media and the inhibition effect enhances with increasing the DILE concentration. Electrochemical parameters attained by Tafel extrapolation, corrosion current density(I_{corr}), Tafel slopes(β_a and β_c) and corrosion potential (E_{corr}) are presented in Table 3. The inhibition efficiencies of DILE in concrete pore solution are also shown in Table 3. The inhibition efficiency (IE) is calculated as:

$$IE(\%) = 100\times(I_{corr} - I_{corr}^{*})/ I_{corr} \quad (2)$$

Where I_{corr} and I_{corr}* are the values of corrosion current density with and without DILE inhibitor, respectively. Increasing the inhibitor concentration reduces the corrosion current density. The presence of DILE inhibitor results in a small shift of the E_{corr} toward active directions in comparison to the result obtained without inhibitor. The reduction in both thecathodic and anodic densities in concrete pore solution shows that the DILE inhibitor suppresses both the cathodic and anodic reactions which can be related to the presence of DILE on carbon steel surface. Furthermore, in the presence of DILE inhibitors the values of β_a were altered more than β_c values which indicate that the anodic reactions were controlled mainly than cathodic reactions in all concentrations. Given that the changes in β_a values ismore considerable than the change in β_c values, it is shown that the DILE inhibition effect are anodic dominating. These results propose that the considered inhibitor acts as a mixed-type inhibitor [21]. It is found that the EI increases with increasing inhibitor concentration. Highest inhibition efficiency obtained in concrete pore solution with 100 mg/L of DILE. Moreover, these findings reveal that I_{corr} reduces with increasing DILE inhibitor concentration, and the addition of DILE cannot vary the values of β_c and E_{corr}. All the results achieved from EIS and polarization studies are in good accordance with together.

Table 3. Electrochemical parameters attained by Tafel extrapolation

DILE contents	I_{corr} (µA/cm^2)	E_{corr}(V)	β_a (mV/decade)	β_c (mV/decade)	IE (%)
0 mg/L	62	-438	104	176	-
10 mg/L	13	-432	65	155	78
50 mg/L	9	-428	53	151	85
100 mg/L	3	-421	55	163	96

Table 4 indicates the comparison of IE% of various green inhibitors in concrete pore solution for corrosion behavior of carbon steel. The findings revealed that the IE of DILE inhibitor in corrosion resistance of Q235 carbon steel was comparable with other inhibitors achieved from previous studies.

Figure 5 shows the FESEM images of Q235 carbon steel into the concrete pore solution with various concentration of DILE inhibitor after immersion time of 18 h at temperature of 25^o. The surface of carbon steel plate immersed in concrete pore solution with 100 mg/L of DILE inhibitor revealed thin pits and low corrosion products, showing a slight pitting corrosion formed on the surface of carbon steel, which is consistent with the results achieved from electrochemical assessments.

Table 4. The comparison of IE% of various green inhibitor in concrete pore solution for corrosion behavior of carbon steel

Inhibitors	Environments	IE (%)	Ref.
Kalanchoeblossfeldina	polluted NaCl	86.8	[22]
Nettle leaves	3.5% NaCl solution	95.0	[23]
Myrmecodiapendans	3.5% NaCl solution	79.7	[24]
Juglansregia	3.5% NaCl solution	94.0	[25]
Chitosan oligosaccharide derivatives	3.5 wt.% NaCl CO_2-saturated solution	84.6	[26]
DILE	Concrete pore solution containing chloride ions	96.0	This work

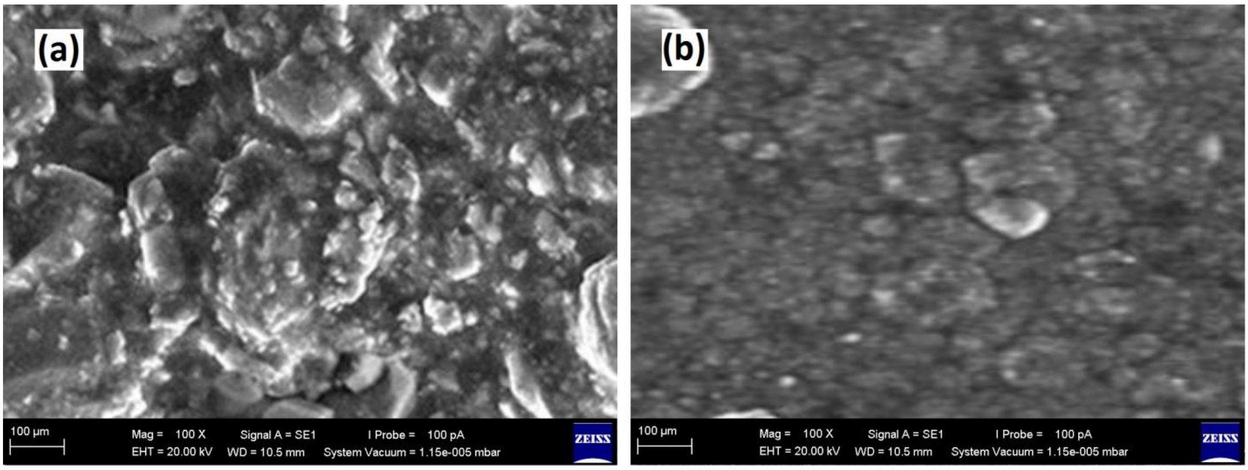

Figure 5. FESEM images of Q235 carbon steel into the concrete pore solution containing chloride ions (a) without and (b) with 100 mg/L DILE inhibitor after immersion time of 18 h at temperature of 25^o.

4. CONCLUSIONS

Corrosion is one of the biggest problems in durability of steel materials.In this work, corrosion resistance of Q235 carbon steel plates in concrete pore solution with various DILE inhibitors were studied using potentiodynamic polarization and EIS analysis. Electrochemical results revealed that the DILE was an effective corrosion inhibitor in decreasing the corrosion behavior of carbon steel at the optimal dosage of 100 mg/L inhibitor. The R_{ct} values were significantly reduced from 56845 Ω to 474208 Ω, as content of DILE inhibitor increased in the concrete pore solution which indicated that the presence of DILE caused to improve the corrosion resistance of Q235 carbon steel. The potentiodynamic polarization results indicate that the DILE was a mixed-type inhibitor that enhanced the performance of corrosion resistant in carbon steel plate considerably with formation an organic layer to restrain both the anodic and the cathodic reactions. The surface morphology of carbon steel plate immersed in concrete pore solution containing 100 mg/L DILE inhibitor revealed the formation of low corrosion products on steel which was in agreement with the results achieved from electrochemical assessments.

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