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Short Communication

Evaluation of Corrosion Inhibition Effect of white mulberry leaves extract on HRB500 Carbon Steel in Alkaline Chloride Solutions

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Corrosion resistance of HRB500 carbon steel in alkaline environment with various inhibitor and NaCl concentrations were investigated using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and scanning electron microscope. The inhibition effect of white mulberry leaves extract (WMLE) on carbon steels in alkaline media were studied. Results revealed that inhibitor and chloride values played a significant role in the formation of protective passive layers on the steel surface. The EIS analysis is in agreement with the best-fit results for double-layer capacitance of solution–steel interface which were steadily increased over 126.5 μFcm^{-2} with 4 wt% NaCl in the alkaline solution, indicating that produced corrosion can occur on the steel surface. Results achieved from electrochemical analysis indicated that a high value of inhibition efficiency (88%) was obtained in the presence of 400 mg/L WMLE at room temperature.

Keywords: Green corrosion inhibitor; Alkaline environment; Electrochemical corrosion behavior; Electrochemical impedance spectroscopy

1. INTRODUCTION

Corrosion has affected many industries and led to major economic losses which need further evaluation to advance corrosion conditions [1]. 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 [2, 3]. Alkaline solutions are the most corrosive into the nature for carbon steel alloys than the other corrosive environment [4]. Thus, it is desirable to investigate the protection of corrosion steels in alkaline solutions. The corrosion resistance of carbon steel depends on the stability and the presence of oxide film on its surface [5, 6].

However, the oxide film formed on the surface of the steel protects it in corrosive environments such as alkaline and acidic solutions. In solutions containing chloride particularly, this oxide layer is damaged and the metal corrodes [7, 8]. Some methods have been applied to decrease the corrosion of steel and its alloys. The use of various Coatings, anodizing and inhibitors (organic and mineral) are the most common techniques of protection [9, 10].

Plants are known as a source of natural compounds with relatively complex molecular structures and different degrees of biological, chemical and physical properties [11]. Extensive research has been done on using plant extracts as inhibitors of corrosion [12]. The inhibition influence of green products extracted from leaves of plant had been reported by some researchers [13]. The white berry belongs to the family of Moraceae that generally grows in Asia. White mulberry leaves consists of phenolic substances namely flavonoids and phenolic acids such as caffeoylquinic acids, caffeic acid, kaempferol-3-O-(6-malonyl)-glucoside, quercetin-3-O-glucoside, cinnamic acid derivatives, quercetin-3-O-(6-malonyl)-glucoside and flavonols [14]. Most of the compounds appear to be operative corrosion inhibitors in metals exposed to an aggressive environment.

Although, many studies had been carried out to investigate green corrosion inhibitor for carbon steels, the white mulberry leaves has never been evaluated as an inhibitor of steel corrosion in alkaline solution. Therefore, this study intended to study the effect of white mulberry leaves extract (WMLE) as a novel green inhibitor for carbon steel corrosion in alkaline environments. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were used to investigate the electrochemical corrosion behavior of HRB500 carbon steel in alkaline solution with different chloride and inhibitor concentrations.

3. MATERIALS AND METHODS

White mulberry trees are native to China. The white mulberry leaves (WML) was washed by tap water and dried in the shade. It was then powdered into small particles. After that, 7 g of powdered WML were mixed with a half litter of DI water at a magnetic induction stirrer for two hours at 80 °C. Then, the prepared solution was filtered using a filter paper. The filtered solution was stirred again at 80 °C for 24 h to become a concentrated solution. Then, the high-viscosity brown gel was attained and powdered. Finally, the achieved powder was utilized as corrosion inhibitor in all tests.

In this study, HRB500 carbon steel with 2cm diameter were utilized to investigate the corrosion resistance of carbon steel rebar in alkaline solution. Table 1 shows the chemical composition of HRB500 carbon steel.

Table 1. Chemical composition of HRB500 carbon steel (wt%)

C	Mn	Si	P	S	Fe
0.20	1.50	0.55	0.03	0.025	Residual

The specimens were polished and cleaned by silicon carbide papers. All steel bars were immersed in acetone solution and washed by DI water.

All experiments were done in an alkaline solution containing KOH 0.6 ML^{-1}, $Ca(OH)_2$ 0.01 ML^{-1} and NaOH 0.2 ML^{-1}. $NaHCO_3$ solutions was used to adjust pH at 13.5.

The experiments were performed in 200mL of 1M alkaline solution with 0, 50, 200 and 400 mg/L of WMLE and 0, 1, 2 and 4 wt% NaCl at 25 °C.

An electrochemical cell was utilized to investigate the electrochemical behavior of the steel rebars. The steel specimens, graphite and saturated calomel electrodes were used as working counter and reference electrodes, respectively. Before analyzing the specimens, all steels were dipped in the electrolyte solution for 24 hours. EIS measurements were done at the frequency range of 0.1 MHz to 0.1 mHz. The potentiodynamic polarization test was conducted in the potential ranges of -0.9 to -0.2 V at scanning rate of 1 mV/s. The surface morphology of the steel rebars was considered by FEI Sirion 200 scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

EIS analysis were done in order to evaluate the electrochemical behaviour of HRB500 carbon steel without and with chloride ions in alkaline media and taken after 24 h immersion time. However, previous reports had studied this subject, there is still disagreement about the EIS response of low carbon steels in alkaline solution at the presence of chlorides.

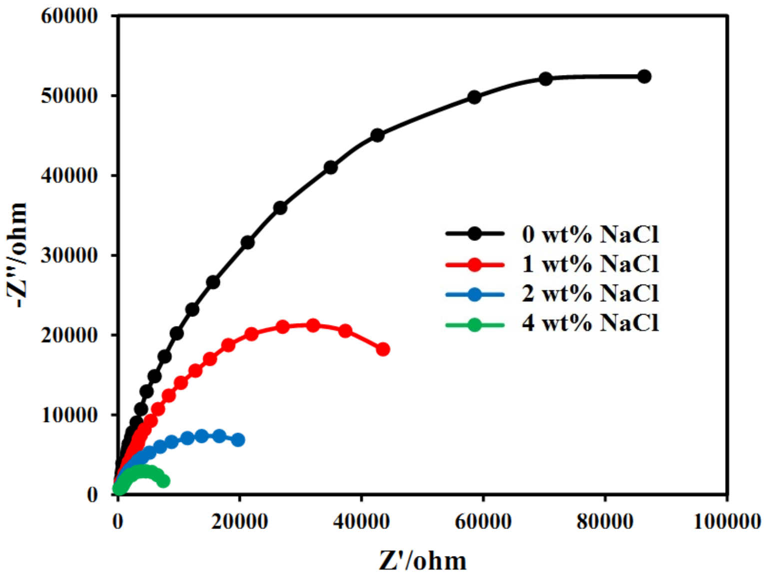

Figure 1. EIS diagrams of HRB500 steels into the alkaline solution with different content of NaCl and without inhibitor after exposure time of 24 h at room temperature.

The Nyquist plots of EIS attained in artificial seawater with different concentrations of NaCl is indicated in Fig. 1. Nyquist plots typically show a capacitive loop that its diameter decreases as the NaCl concentrations increase which can be associated to the corrosion resistance of chloride ions on the steel surface. The EIS plot shows the resistance between the electrolyte solution and the working electrode at the high-frequency. Furthermore, at low-frequency, it can be related to the charge-transfer resistance into the corrosion process [15].

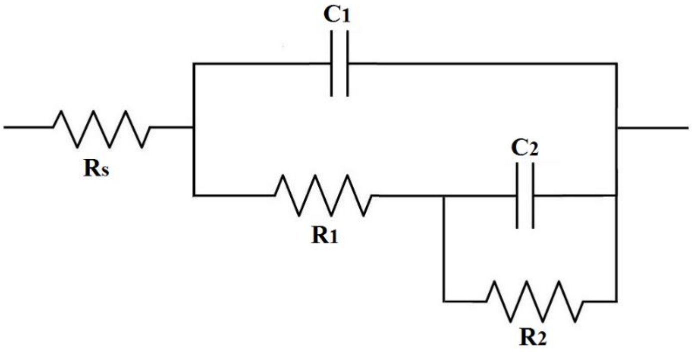

Figure 2. The equivalent circuit model

Figure 2 reveals an equivalent circuit model with two time constants that proposed to simulate the EIS process of steel rebars in this study.

At higher frequencies, R_1 and C_1 show a resistance because of the ionic paths by the oxide film and capacitive behavior of formed passive layer, respectively [16]. At the second time constant, R_2 and C_2 reveals the charge-transfer resistance and the capacitive behavior in the interfaces [17]. The best fitting parameters based on the circuit depicted in figure 2 are summarized in Table 2. As shown, the R_2 values are significantly decreased from 146585 Ω to 7261 Ω, as NaCl concentration increases in the alkaline solution which show that the presence of chloride ions caused to enhance the corrosion behavior of the steel.

Table 2. EIS parameters derived from the fitting equivalent circuit for HRB500 steels into the alkaline solution with different content of NaCl and without inhibitor after exposure time of 24 h at room temperature

Concentration of NaCl	R_s (Ω cm^2)	R_1(Ω cm^2)	C_1(μF cm^{-2})	R_2 (Ω cm^2)	C_2 (μF cm^{-2})
0 wt%	75.9	106784	14.7	146585	21.6
1 wt%	68.4	48585	39.4	56845	68.6
2 wt%	73.5	19743	58.7	29632	90.4
4 wt%	78.7	4859	86.5	7261	126.5

Furthermore, table 2 exhibits that R_1 gradually reduced by increasing the NaCl concentration which indicates that porous products and non-protective corrosion had been enhanced on the steel surface. These findings were consistent with the best-fit results for C_2 which were gradually increased over 126.5 μFcm^{-2} with 4 wt% NaCl in the alkaline solution, indicating that corrosion can happen on the steel surface [18].

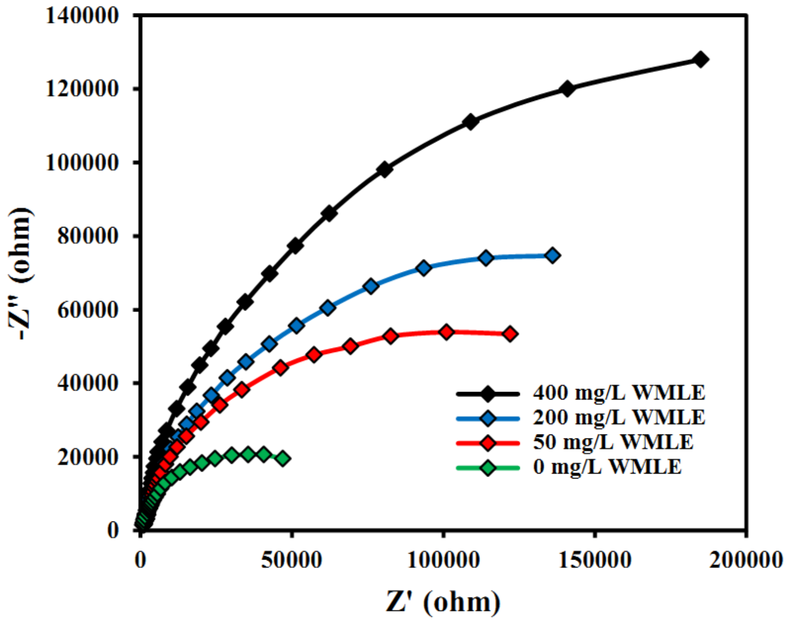

Figure 1. EIS diagrams of HRB500 steels into the alkaline solution with different concentration of WMLE inhibitor and 1 wt% NaCl at after exposure time of 24 h at room temperature.

The Nyquist plots after exposure time of 24 h with different concentration of WMLE inhibitor are revealed in Figure 3.

As shown, the sample were immersed to the alkaline solution without inhibitor indicated one whole half semicircle loop and the sample that was exposed to the alkaline solution with WMLE revealed an incomplete semicircle loops and larger radius than the one without inhibitor, indicating a superior corrosion resistance behavior of the inhibitor. When the inhibitor concentration increased, the semi-circle loop diameter increased because of the formation of passive layer or adsorption of WMLE in anodic site of HRB500 carbon steel and therefore reduced the iron dissolution [19]. The passive film decreased the attack of chloride ions on the surface of steel rebar and efficiently control the pitting corrosion.

The best fitting parameters based on the equivalent circuit (Fig. 2) are summarized in Table 3. As shown, the R_2 values were significantly decreased from 56845 Ω to 474208 Ω, as concentration of WMLE inhibitor increased in the alkaline solution which showed that the presence of WMLE caused to enhance the corrosion resistance of the carbon steel.

Table 3. EIS parameters derived from the fitting equivalent circuit for HRB500 steels into the alkaline solution with different concentration of WMLE inhibitor and 1 wt% NaCl after exposure time of 24 h

Inhibitor amounts	R_s (Ω cm^2)	R_1(Ω cm^2)	C_1(μF cm^{-2})	R_2 (Ω cm^2)	C_2 (μF cm^{-2})	IE (%)
0 mg/L	68.4	48585	39.4	56845	68.6	0
50 mg/L	78.3	114526	14.4	210435	21.9	73
200 mg/L	83.6	136524	10.7	275870	15.8	79
400 mg/L	85.8	297420	6.5	474208	9.45	88

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

$$IE\ (\%) = 100 \times (R_2 - R_2^*)/ R_2 \qquad (1)$$

where R_2 is the charge-transfer resistance with inhibitor and R_2^* the charge-transfer resistance without inhibitor.

Table 4 shows the IE comparison of different inhibitor extracted from plants as mentioned in the literature. The results indicated that the IE of WMLE inhibitor for corrosion resistance of carbon steel were comparable with other inhibitors obtained from the literature.

Table 4. IE Comparison of different inhibitor extracted from plants for corrosion inhibitor of carbon steel

Inhibitors	Environment	IE (%)	Ref.
Motrilin	HCl	68.9	[20]
Eucalyptus Globulus	Alkaline chloride solution	87.6	[21]
Lemon verbena leaves	H_2S	92.5	[22]
ZnA-CIL.L	Aqueous chloride solution	93.0	[23]
Seaweed	Saline formation water	93.5	[24]
WMLE	Alkaline Chloride Solutions	88.0	This work

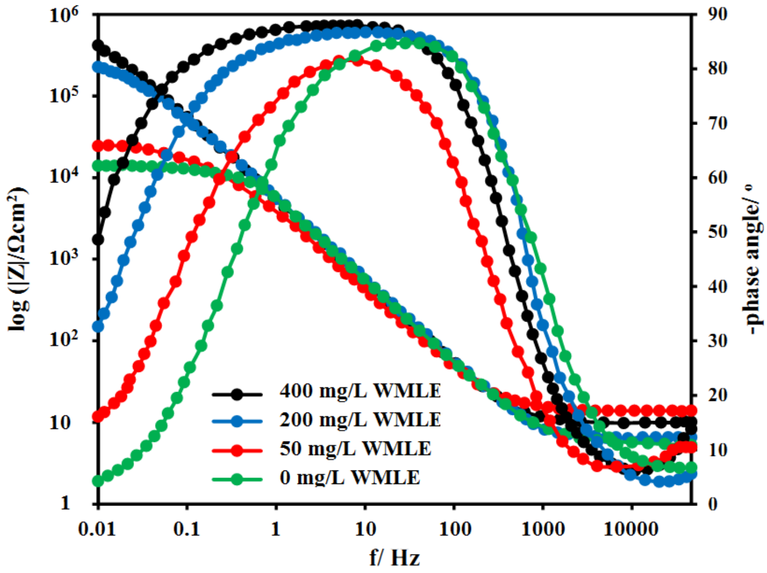

Figure 4. Bode plots of the specimens immersed in alkaline environment with different concentration of WMLE inhibitor and 1 wt% NaCl after exposure time of 24 h

Figure 4 shows the Bode plots of the specimens immersed in alkaline environment with different concentration of WMLE inhibitor after exposure time of 24 h. As shown, when inhibitor amounts were increased from 0, 50, 200 and 400 mg/L, the impedance values improved 8 times. This result proposed that high amount of WMLE inhibitor remarkably control the corrosion of the carbon steel rebar in alkaline solution. It can be attributed to whole cover the active surface of carbon steel rebar by WMLE inhibitor [25]. Furthermore, it can be related to the formation of passive layer on steel surface by adsorption of synthesized inhibitor. The layer is stronger where the chloride ions do not affect the passive properties of the layer. The samples immersed in the solution without inhibitor were more sensitive to corrosion because of chloride ions attack on the surface of the steel rebar. Consequently, reduction in impedance value was found in solutions containing inhibitor. As shown in figure 4, the maximum phase angle for a solution containing an inhibitor at a lower frequency was shifted to a higher angle due to the creation of protective passive layer [26]. The phase angle was shifted from -87° to -89° in solutions with 200 and 400 mg/L inhibitor, indicating that the passive layer was uniform and homogenous.

Figure 5 indicates the WMLE inhibitor influence on corrosion behavior of carbon steel in alkaline solution. Adding inhibitors to alkaline solution had affected the reactions of corrosion and can be documented through the variations in both cathodic and anodic polarization plots as well as shifted into the corrosion potentials. The inhibitor addition shifted the corrosion potential to the more negative values. Moreover, polarization analysis indicated that the slope of polarization plots had changed slightly with the addition of inhibitors in alkaline solutions, showing that inhibition process was similar at all the inhibitor concentrations.

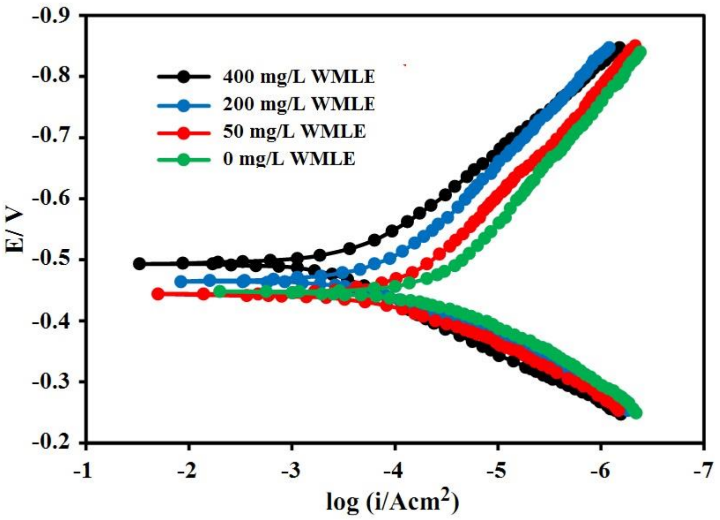

Figure 5. Polarization curves of steel samples in alkaline solution with different concentration of WMLE inhibitor and 1 wt% NaCl after exposure time of 24 h

i_{corr}, E_{corr} and slopes of cathodic and anodic polarization curves (β_c and β_a) were attained by fitting the Tafel polarization plots which are listed in Table 3. The trend of variations in E_{corr} values made the facts better revealed by the initial evaluation of the polarization plots. As shown, in 50 mg/L inhibitor, E_{corr} of steel shifted toward anodic direction and then with increasing inhibitor concentration, E_{corr} moved to the cathodic direction. The value of potential changes was 48 mV, which confirmed that the WMLE acted as an inhibitor for steel corrosion in alkaline solution [27, 28]. Moreover, Table 3 revealed that the values of β_c were higher than the values of β_a at all concentrations of inhibitor. Furthermore, the changes in β_c value with increasing inhibitor content was greater than that of β_a values.

Table 3. Corrosion parameters attained by fitting the Tafel polarization plots of steel samples in alkaline solution with different concentration of WMLE inhibitor and 1 wt% NaCl after exposure time of 24 h

WMLE concentration	**Corrosion current density (μAcm^{-2})**	**Corrosion potential (mV)**	**-β_c (mVdec^{-1})**	**β_a (mVdec^{-1})**
0 mg/L	232	-446	192	93
50 mg/L	141	-439	223	87
200 mg/L	63	-468	161	81
400 mg/L	29	-494	126	87

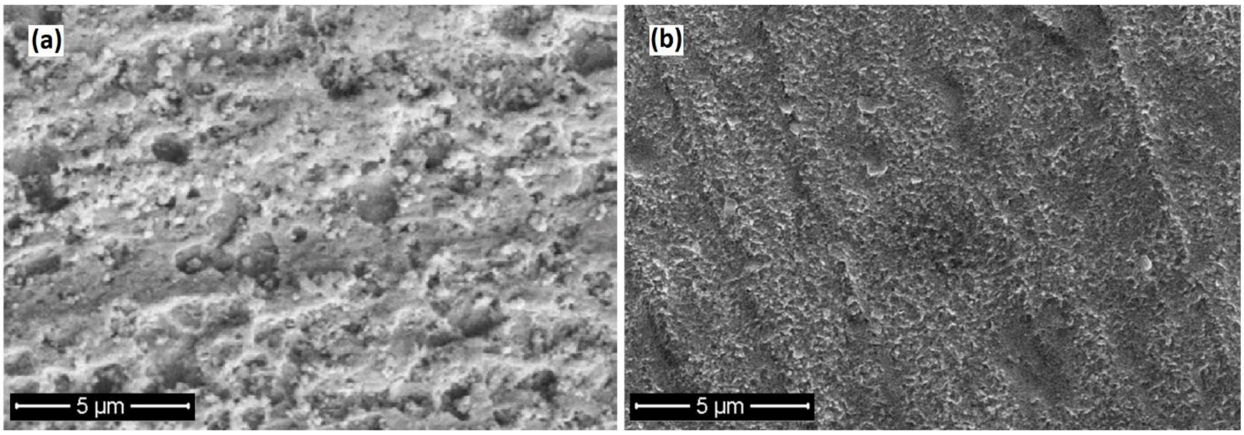

Figure 6. FESEM images of HRB500 steel after 24 hours exposed to alkaline solution with 1 wt% NaCl and (a) without and (b) with 400 mg L^{-1} WMLE inhibitor

Figure 6 shows the surface morphology of HRB500 steel after 24 hours exposed to alkaline solution without and with 400 mg L^{-1} WMLE inhibitor. During the exposure of the steel in blank alkaline solution, the fast reactions of aggressive corrosion damaged the steel surface seriously which led to highly rough surface as indicated in Figure 6a. However, the WMLE inhibitor affected the corrosion behavior of HRB500 steel in alkaline solution and significantly reduced the corrosion rate (Fig. 6b). Consequently, less damage of the carbon steel had confirmed the inhibition properties of WMLE.

4. CONCLUSIONS

Corrosion resistance of HRB500 carbon steel in alkaline environment with various inhibitor and NaCl concentrations were investigated using EIS, potentiodynamic polarization, and FESEM. The inhibition effect of WMLE on carbon steels in alkaline media were studied. Results reveal that inhibitor and chloride values play a significant role in the creation of protective passive layers on the steel surface. The EIS analysis is in agreement with the best-fit results for double-layer capacitance of solution–steel interface which were steadily increased over 126.5 μFcm^{-2} with 4 wt% NaCl in the alkaline solution, indicating that produced corrosion can occur on the steel surface. The charge-transfer resistance values were significantly decreased from 146585 Ω to 7261 Ω, as NaCl concentration increased in the alkaline solution which showed that the presence of chloride ions caused to enhance the corrosion behavior of the steel. The polarization measurement indicated that the value of potential changes was 48 mV, which confirmed that the WMLE acted as an inhibitor for steel corrosion in alkaline solution. Results achieved from electrochemical analysis indicated that a high value of inhibition efficiency (88%) was obtained in the presence of 400 mg/L WMLE at room temperature.

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