



Effect of L-Citrulline from Watermelon Seed Extract as a Green Corrosion Inhibitor against the Corrosion Rate of Pipe Steel API 5L X65

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Abstrak. API 5L X65 carbon steel is used in many industries, especially as oil and gas pipelines. However, this carbon steel pipe is vulnerable to corrosion at the inner surface owing to the flow of oil that is a multiphase system and contains dissolved salts. The corrosion phenomenon of the internal surface can be prevented by using an inhibitor. Most of the inhibitors used in industry are composed of compounds that are toxic and environmentally unfriendly. Consequently, the use of a natural inhibitor is at the forefront of corrosion inhibition studies. This study examines the efficiency of watermelon seed extract as an inhibitor before and after the addition of methyl ethyl glycol (MEG). The influence of L-citrulline from watermelon seed extract (WMSE) and MEG on the inhibition of corrosion of carbon steel in 3% NaCl containing acetic acid saturated by CO₂ at room temperature was investigated by the immersion test, polarization test, electrochemical impedance spectroscopy (EIS), and surface analysis by scanning electron microscopy (SEM). According to the experiment results, the corrosion rate increased with the acid concentration and the effect of CO₂. The corrosion rate can be inhibited by MEG, WMSE, and mixtures thereof. In comparison with 3% NaCl media containing acetic acid (HAc) 3360 ppm in saturated CO₂ at room temperature, the inhibition efficiency of WMSE using polarization and EIS methods were 93.54% and 95.89%, respectively. However, based on the immersion test results, the inhibition efficiency was decreased. The inhibition efficiency of WMSE dropped after 120 hours of the immersion process by almost 40fold to 2.38%, while the efficiency of MEG was able to inhibit the surface by 80.48%. The mechanism of the inhibition by a WMSE molecule is through a chemisorption process, which forms a complex bond and generates a passive layer of Fe-WMSE

Keyword: citrulline, corrosion, electrochemical impedance spectroscopy, green inhibitor, methyl ethyl glycol.

1 Introduction

Corrosion is a serious problem throughout the oil and gas industries, where inhibitor usage has increased to delay the attack on metals in aggressive environments [1]. However, the use of toxic inhibitors is

damaging to the environment [2]. Therefore, research to discover natural products that are able to act as inhibitors is being conducted [3-5]. The use of methyl ethyl glycol (MEG) as a corrosion inhibitor in a CO₂-saturated solution has previously been researched, but requires 50–70% volume to be efficient; therefore, MEG is not an efficient inhibitor [6]. A study on watermelon seed extract (WMSE) as a corrosion inhibitor showed an efficiency of 83% at 2 ppm in an HCl solution [7].

Therefore, WMSE as a corrosion inhibitor is compared with the MEG inhibitor under the same conditions. Corrosion inhibition of API 5L X65 steel in a CO₂-saturated 3% NaCl solution by WMSE has been evaluated by the mass-loss method, electrochemical studies, and polarization test. The purpose of this study is:

- i) To evaluate the mechanism and inhibition efficiency (IE) of WMSE using immersion, EIS, and polarization test methods.
- ii) To compare the IE of WMSE with that of MEG in a CO₂-saturated 3% NaCl medium.
- iii) To analyze the synergic effect of WMSE and MEG.

2 Experimental Procedure

2.1 Preparation of Watermelon Seed Extract

The seeds were separated from the fruit, dried, and crushed into powder. The powder (5 g) was added to 1 M HCl (1 L) solution and heated to 60°C for 10 minutes. The solution was filtered so the residue of watermelon seed remained. The same dilution process was repeated and then mixed with NaCO₃. The final step was to add ethyl acetate to obtain solidified citrulline.

2.2 Weight-loss Method

API 5L X65 steel was cut into coupons with dimensions of 5 × 2.5 cm and then weighed. The coupons were immersed in CO₂-saturated 3% NaCl (300 mL) for 24 hours. After 24 hours, the coupons were washed, dried, pickled and then weighed using an analytical balance.

2.3 Electrochemical Impedance Spectroscopy (EIS) Method

Electrochemical Impedance Spectroscopy was performed using a three-electrode system. A total of 3% NaCl (300 mL) was used as a blank in the cell chamber. Working Electrode (API X65), Saturated Calomel Electrode, and Platinum Electrode were immersed in the test solution, which was bubbled with CO₂ gas for 2 hours. After 1.5 hours, the electrode was connected to the potentiostat (VersaSTAT 3) for measurements [8]. The same procedure was used for WMSE and MEG.

The EIS measurement was conducted at respective open circuit potential, in a frequency range from 10-MHz to 10-kHz with a sinewave perturbation amplitude of 10-mV using VersaSTUDIO software.

The corrosion inhibition efficiency (IE) from the impedance spectroscopy measurements were estimated by comparing the charge transfer resistance with (R_{ct}) and without (R_{ct}^0) WMSE using the expression given in,

$$I E = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad \% \quad (1)$$

The same order of corrosion inhibition efficiency was observed in the experiment where the polarization resistance (R_p) using Eq. (2)

$$I E = \frac{R_p - R_p^0}{R_p} \times 100 \quad \% \quad (2)$$

where R_p and R_p^0 represent the polarization resistance in the presence and absence of WMSE respectively.

2.4 Polarization Test

This method, in general, was used for determining the corrosion rate of metal in certain conditions [9]. A total of 3% NaCl (300 mL) was used as the blank and was bubbled with CO₂ gas for 2 hours. After measurements of the blank were completed, the process was repeated for the acetic acid, MEG, and WMSE solutions. The measurements were conducted at room temperature using the VersaSTAT 3 software.

Anodic Tafel slopes (β_a) and cathodic Tafel slopes (β_c) obtained from the extrapolation of the linear Tafel regions of the polarization curves along with other electrochemical parameters such as corrosion rate (CR), corrosion current density (I_{corr}) and corrosion potential (E_{corr}) [7]. The I_{corr} values are found to decrease as the concentration of the extracts increased. The inhibition efficiency (IE) was calculated from the values of corrosion current density in the absence (I_{corr}^0) and presence (I_{corr}) of the inhibitors using Eq. (3).

$$I E = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100 \quad \% \quad (3)$$

2.5 Scanning Electron Microscope (SEM) Surface Analysis

API 5L X65 Steel was cut into dimensions of 1 × 1 cm, ground, and polished using alumina paste until a mirror finish was achieved. The weight was recorded, then the steel was immersed in CO₂-saturated 3%

NaCl (300 mL) for 24 hours, and then the exposed samples were observed by SEM.

3 Results and Discussions

3.1 Polarization Tests

3.1.1 Influence of Acetic Acid on Polarization Test Results

According to the test result, the potential curve showed that the corrosion potential was bent towards a more positive potential after adding 3360 ppm of acetic acid (HAc), as shown in Figure 1. The corrosion rates before and after adding the acetic acid were 5.59 mpy and 48.96 mpy, respectively. This meant that adding acetic acid increased the corrosion rate of carbon steel [10]. This was caused by the increase of hydrogen ions in the solution [11].

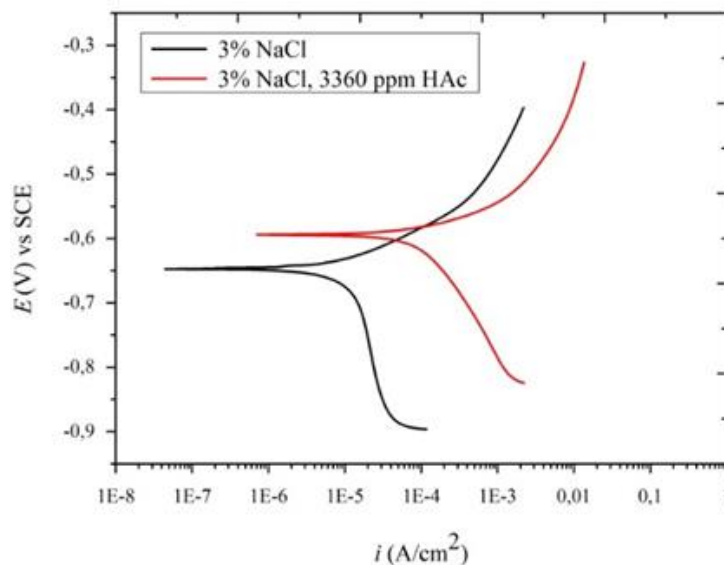


Figure 1. Polarization curve of carbon steel, black line represents the absence of acetic acid, and orange line represents the presence of acetic acid

3.1.2 Influence of CO₂ on Polarization Test Results

The results showed that CO₂ increased the corrosion rate in both NaCl and acetic acid solutions. In NaCl, the oxidation reaction at the anodic site was aggressively increased because the CO₂ formed H₂CO₃, which is also acid, therefore increasing the concentration of H⁺ ions. Figures 2 and 3 show the effect of CO₂ in various acid solutions.

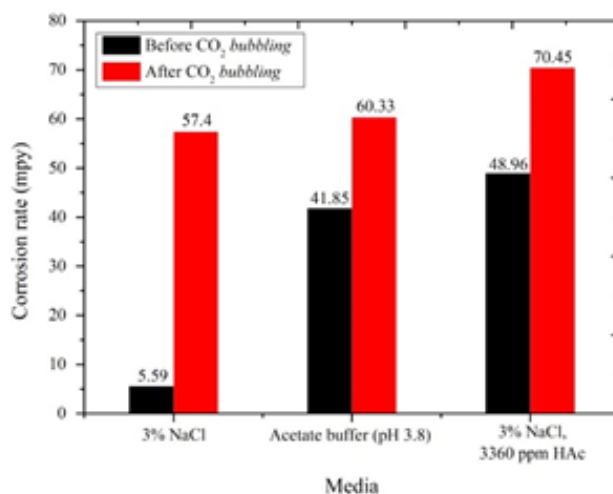


Figure 2. Effect of the presence of CO₂ on the corrosion rate. Black bars represent the absence of CO₂ and red bars represent the presence of CO₂.

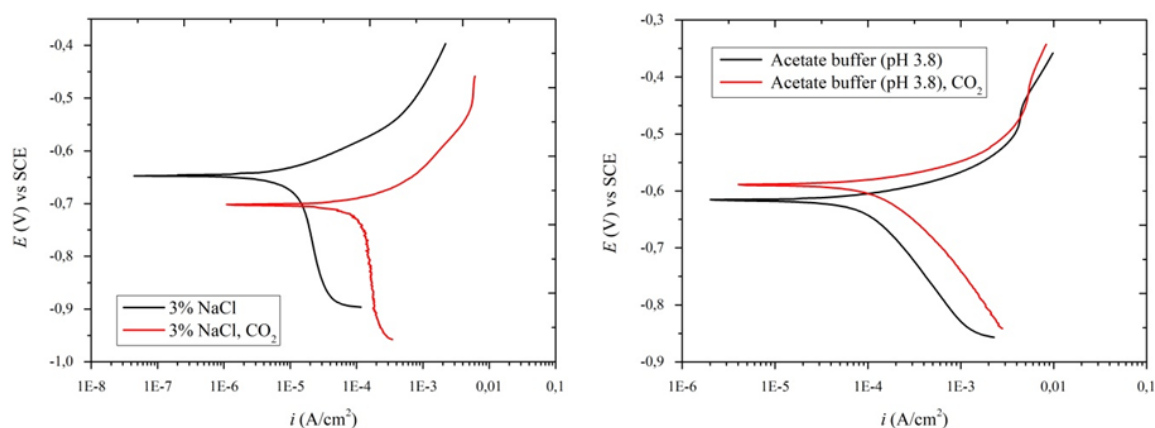


Figure 3. Effect of CO₂ on the polarization curve. (a) E_{corr} of steel in NaCl solution. (b) E_{corr} of steel in buffer acetate solution.

3.1.3 Influence of MEG Polarization Test Results

In this study, 50%v of MEG was added to the test solution, which resulted in an increase of the corrosion potential towards the positive side in NaCl, but towards the negative side in the acetic acid solution, which is shown in Figure 4. It is possible that MEG inhibits Cl⁻ activity, therefore, reducing the oxidation reaction at the anode. In the acetic acid solution, MEG slowed the reaction of H⁺. In conclusion, MEG was capable of preventing hydrogen from reacting with CO₂, thereby reducing the amount of H₂CO₃ formed [12]. The inhibitor efficiency was improved by the presence of MEG as shown on Table 1.

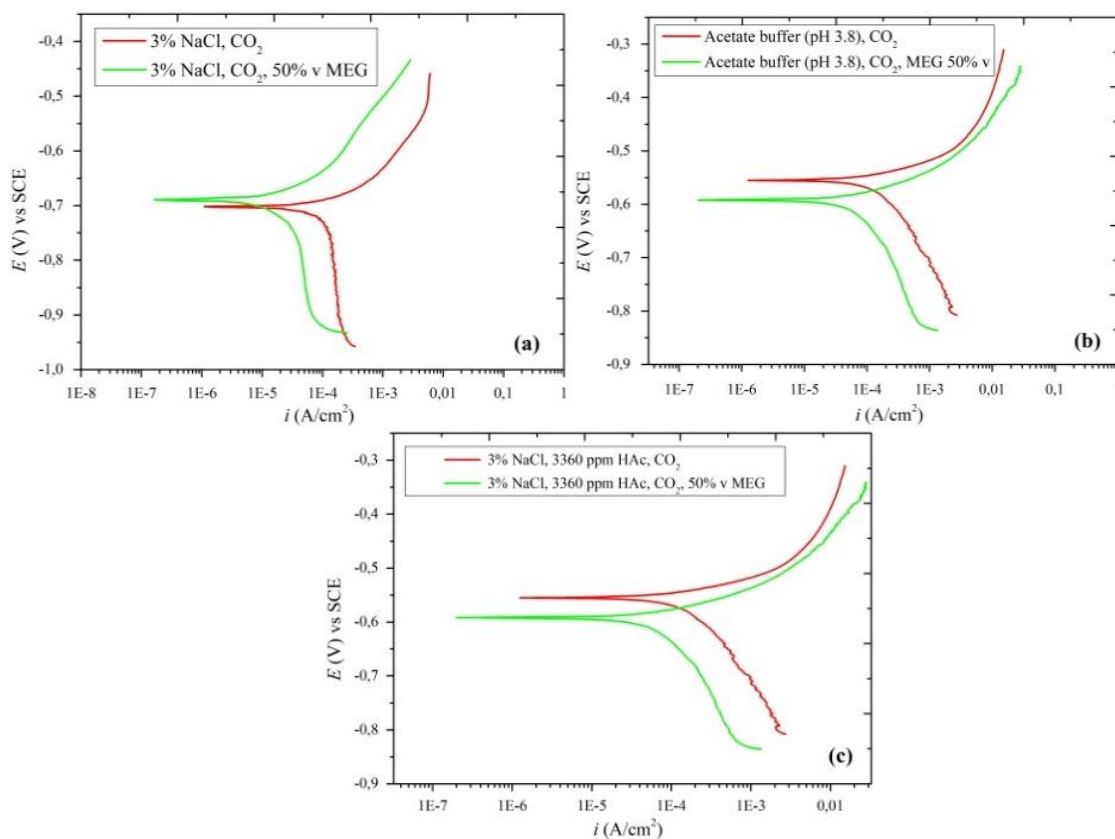


Figure 4. Effect of MEG in NaCl (a), acetic acid buffer (b), and NaCl 3360 ppm of HAc (c). Green line represents the presence of CO₂ in the solution.

Table 1. Effect of MEG 50%v on corrosion rate of carbon steel in acidic solution

Acid solution	Corrosion rate with CO ₂ (mpy)		Inhibitor efficiency (IE, %)
	Without MEG	With MEG	
3% NaCl	57.4	16.19	71.79
Acetic acid buffer (pH 3.8)	60.33	33.50	44.47
3% NaCl, HAc 3360 ppm	70.45	29.93	57.51

3.1.4 Influence of Watermelon Seed Extract on Polarization Test Results

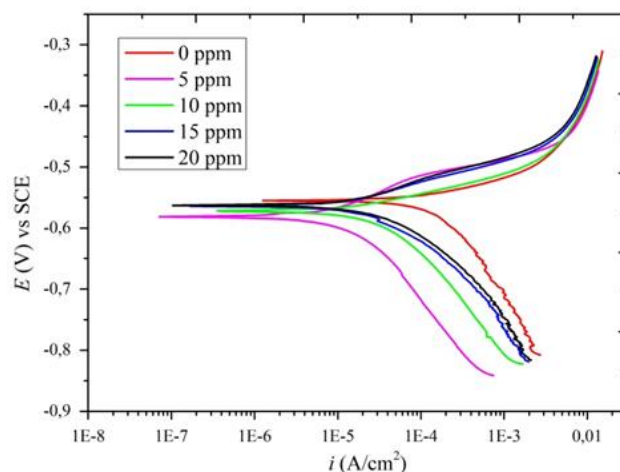


Figure 5. Polarization curve in the presence of watermelon seed extract in various concentrations

The test using WMSE (5–20 ppm) resulted in maximum efficiency of 93.54% with 10 ppm. The polarization test in Figure 5 shows the tendency towards a negative potential, which prevented the reaction at the cathode.

The WMSE also interacted with carbon steel and formed a protective film at the anode [13]. When the concentration was increased to 20 ppm, the corrosion rate also increased as well as inhibitor efficiency as presented in Table 2; therefore, it was important to find the critical concentration of the inhibitor. The test results showed that the anodic gradient was greater than that of the cathode, which confirmed that this was an anodic inhibitor.

Table 2. Effect of watermelon seed extract on corrosion rate in NaCl + HAc 3360 ppm solution

Solution	Concentration of watermelon seed extract (ppm)	Corrosion rate with CO ₂ present (mpy)	IE (%)
3% NaCl +HAc 3360 ppm	0	70.45	-
	5	4.96	90.77
	10	4.55	93.54
	15	7.68	89.09
	20	9.3	86.68

3.1.5 Influence of MEG and Watermelon Seed Extract Mix on Polarization Test Results

The test was also conducted where MEG and WMSE were mixed. According to the polarization curve, the corrosion potential was shifted towards the positive side with the increase of the WMSE concentration. This mixture was more beneficial for MEG, as it increased the IE of MEG, rather than the other way around (Table 3). In NaCl solution, the IE of MEG alone was 57.51% compared with MEG mixed with 5 ppm of WMSE, which exhibited an IE of 77.21%. On the other hand, the increase of WMSE decreases corrosion rate as shown in figure 6.

Table 3. Corrosion rate of carbon steel in the presence of watermelon seed extract and MEG using the polarization test results.

Solution	Watermelon seed extract (ppm)	Corrosion rate with CO ₂ (mpy)	IE (%)
3% NaCl + HAc 3360 ppm	0	70.45	-
3% NaCl + HAc 3360 ppm + MEG	0	29.93	57.51
	5	7.09	77.21
	10	9.91	66.88
	15	10.27	65.68
	20	11.28	72.40

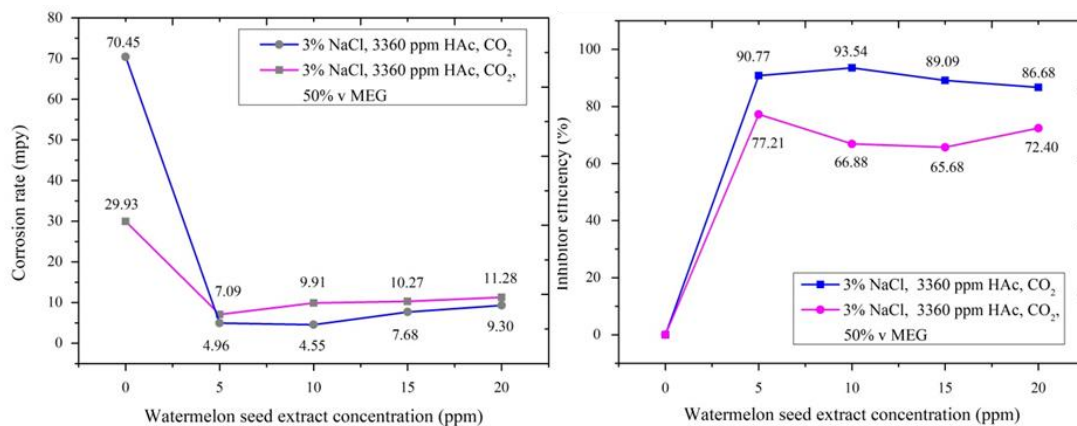


Figure 6. (Left) Corrosion rate of steel in NaCl solution in the presence of watermelon seed extract of various concentrations (blue line) and with MEG + watermelon seed extract (pink line). (Right) Efficiency of watermelon seed extract as an inhibitor in NaCl solution without MEG (blue line) and with MEG (pink line).

3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS was used to analyze the protective film of the inhibitor, using three electrodes (carbon steel X65, graphite, and calomel).

3.2.1 Influence of Watermelon Seed Extract on EIS

The Nyquist curve of carbon steel in 3% NaCl + HAc 3360 ppm with various concentrations of watermelon seed extract is displayed in figure 7. In 3% NaCl + 3360 ppm acetic acid solution as shown in Figure 7, the highest efficiency of 95.89% was achieved for a WMSE concentration of 20 ppm as shown in table 4. In the polarization experiment, the highest efficiency was achieved with a concentration of 10 ppm. Although EIS and polarization results were different, it was still concluded that the WMSE performed well in CO₂ saturated 3% NaCl + acetic acid solution.

Table 4. Inhibitor efficiency on NaCl + HAc 3360 ppm in the presence of WMSE using EIS method

Watermelon seed extract (ppm)	R (kΩ)	IE (%)
0	632.66	-
5	2263.52	72.04
10	2785.33	77.28
15	4474.54	85.86
20	15428.99	95.89

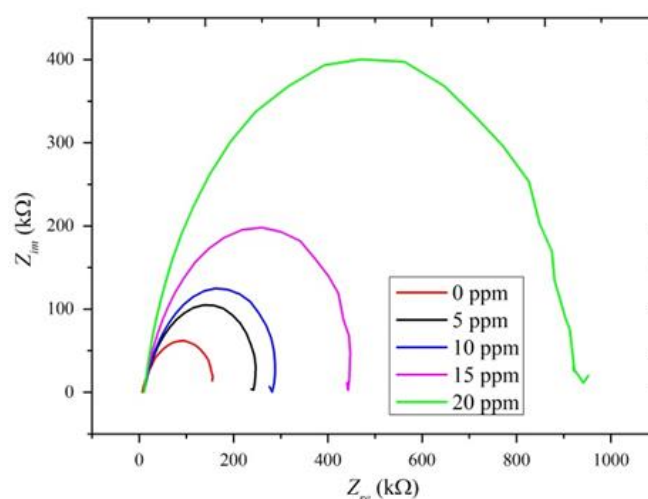


Figure 7. Nyquist curve of carbon steel in 3% NaCl + HAc 3360 ppm with various concentrations of watermelon seed extract.

3.2.2 Influence of MEG and Watermelon Seed Extract Mix on EIS

According to the Nyquist curve displayed on figure 7, the impedance was greater with the increase of the concentration of WMSE in NaCl + HAc 3360 ppm + MEG. It is known that a passive layer is formed, which slows the oxidation reaction. The mixture of MEG and WMSE could achieve an IE of 83.21%, which was lower than the WMSE alone value of 95.89% as shown in figure 8. It is unusual compared to the other condition where the mixed inhibitor will improve the inhibition effect [14].

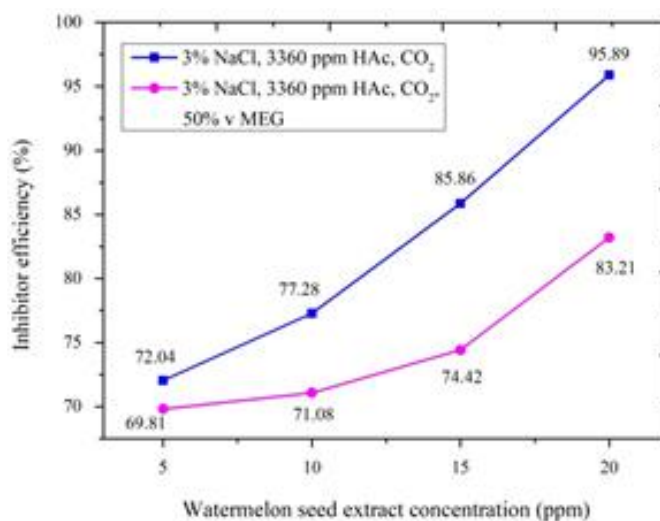


Figure 8. Efficiency of watermelon seed extract inhibitor in NaCl solution without MEG (blue line) and with MEG (pink line).

3.3 Immersion Test

The purpose of the immersion test was to compare the corrosion rate obtained from the polarization test and the weight loss calculation. The parameters of this method were solution composition, temperature, volume, and surface preparation [10]. API 5L X65 steel was immersed in five solutions of various acidities for 24 hours at room temperature (Table 5). It was shown that adding HAc to NaCl increased the corrosion rate. MEG and WMSE were also proven to reduce the corrosion rate with efficiencies of 80.48% and 62.16%. The mixture of both inhibitors yielded an efficiency of 68.03%, which was lower than the result for MEG. The test was then conducted again for 120 hours at room temperature (Table 6). In this experiment, MEG achieved an IE of 72.63%, whereas WMSE only achieved an IE of 2.38%. The mixture of both inhibitors yielded an IE of 64.47%, which was lower than the result

of MEG. It was concluded that in the 5 days of immersion, the ability of WMSE to inhibit the carbon steel was reduced, which may have been caused by the lack of concentration. It is known that if the anodic inhibitor concentration is not enough to cover the whole surface, the corrosion rate is faster than the inhibition rate [9].

Table 5. Immersion test results of various acids in CO₂ for 24 hours.

No.	Solution	Corrosion rate (mpy)	IE (%)
1	3% NaCl	12.26	-
2	3% NaCl, HAc 3360 ppm	21.51	-
3	3% NaCl, HAc 3360 ppm, MEG 50%v	4.19	80.48
4	3% NaCl, HAc 3360 ppm, EBS 10 ppm	8.14	62.16
5	3% NaCl, HAc 3360 ppm, MEG 50%v, EBS 10 ppm	6.87	68.03

Table 6. Immersion test results of various acids in CO₂ for 120 hours

No.	Solution	Corrosion rate (mpy)	IE (%)
1	3% NaCl	18.48	-
2	3% NaCl, HAc 3360 ppm	28.41	-
3	3% NaCl, HAc 3360 ppm, MEG 50%v	7.77	72.63
4	3% NaCl, HAc 3360 ppm, EBS 10 ppm	27.73	2.38
5	3% NaCl, HAc 3360 ppm, MEG 50%v, EBS 10 ppm	10.09	64.47

3.4 Polarization Curve of the Immersion Test Samples

The polarization test was also executed on the same specimens after the immersion test. This test was conducted to compare the results between the two methods. The curve showed that after the immersion process, adding MEG and WMSE shifted the potential to the more negative side. This confirmed that carbon steel became more passive after adding MEG and WMSE. E_{corr} after adding MEG was also much lower than E_{corr} after

adding WMSE as shown in figure 9. According to this result, the MEG solution performed better than the WMSE especially in the solution containing CO₂ and other hydrocarbon compounds [16]. The IE of MEG was 91.30% while that of WMSE was only 40%. The mixture of the two yielded an efficiency of 65.37%. Therefore, the efficiency of WMSE was enhanced after adding MEG, but there was no synergic effect for MEG after adding WMSE.

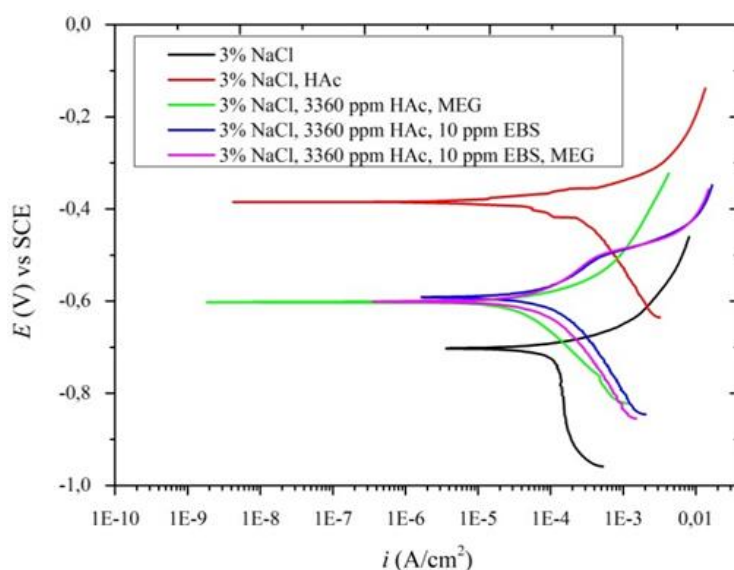


Figure 9. Polarization curve of carbon steel that were immersed for 24 hours in various acid solutions at room temperature

3.5 Scanning Electron Microscope Analysis

X65 carbon steel was immersed in 3% NaCl with and without HAc 3360 ppm for 24 hours and then examined using SEM in figure 10. Figure 10b shows the damage to the metal surface after 24 hours, where at this state, the FeCO₃ layer was not formed perfectly because the Cl⁻ ions still damaged the surface. Figure 11c shows the effect after adding HAc 3360 ppm, where the corrosion product, FeCO₃, was more stable than before, but was not permanent [16], because Ac⁻ ions reacted with Fe²⁺ ions to form Fe(Ac)₂, which has high solubility properties and therefore re-exposed the surface to the corrosive agent. Figure 10d shows the effect of MEG as an inhibitor, where the surface was protected. MEG slowed the reaction of Fe²⁺ ions with both chloride and acetic ions, thereby stabilizing the FeCO₃ passive layer [16]. Figure 11e shows that most of the surface was protected and undamaged, but there were some spots

where the damage occurred, which could be an effect of the immersion time and the lack of seed extract concentration [16]. Figure 10f shows the mixture of MEG and WMSE as an inhibitor, where the surface was more protected than that shown in Figure 10e. This confirmed that MEG was a better inhibitor for a longer duration than WMSE

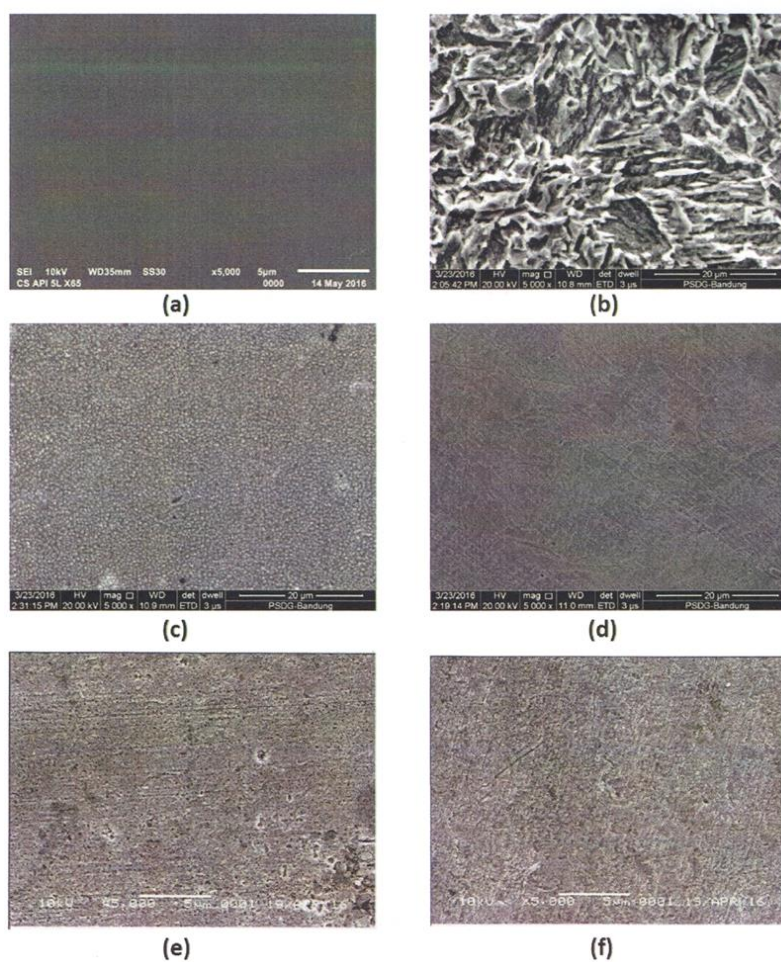


Figure 10. a) Surface of API5LX65 steel before immersion. b) Immersed in NaCl. c) Immersed in NaCl + HAc 3360 ppm. d) Immersed in NaCl + HAc + MEG. e) Immersed in NaCl + HAc + watermelon seed extract. f) Immersed in NaCl + HAc + MEG + watermelon seed extract.

3.6 Watermelon Seed Extract Inhibition Mechanism

The protective mechanism of the WMSE was determined from ΔG_{ads} using the Temkin [13] adsorption equation, which is shown in Table 7.

According to the results, the negative result confirmed that the reaction was spontaneous. WMSE is chemically adsorbed to the surface but physically adsorbed when mixed with MEG [17]. The UV-Vis test also confirmed that there were bonds formed between Fe and WMSE [7]. A free-electron from the seed extract filled the empty orbital of Fe and formed a Fe-seed extract complex bond. There were two suspects from which the other electron that filled the empty orbital originated, oxygen and nitrogen. In this case, the WMSE molecule was not charged; therefore, the most possible reaction was that the molecule was protonated, then donated two free electrons and formed a Fe-seed extract bond as shown in figure 11.

Table 7. Calculation result of the Temkin watermelon seed extract adsorption to X65 carbon steel surface

Added inhibitor	ΔG_{ads} (kJ)
EBS	-47.07
EBS-MEG	-7.47

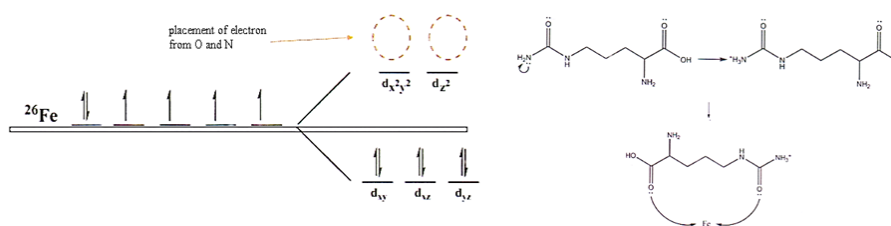


Figure 11 . (Left) Placement of free electron from either oxygen or nitrogen to the D orbital in Fe. (Right) Inhibition mechanism of watermelon seed extract to Fe ions.

4 Conclusion

The present study led to the following conclusions:

- In CO_2 saturated 3% NaCl + 3360 ppm acetic acid medium at room temperature, the IE of WMSE according to Tafel and EIS method were 93.54% and 95.89%.
- The inhibition mechanism of WMSE was chemisorption, which resulted in a complex bond with a free electron (either O or N) and formed a passive film of Fe-WMSE.

- According to the polarization test results, the efficiency of WMSE was higher than MEG at a short time of exposure.
- Inhibition efficiency of WMSE was reduced after 120 hours of exposure because the concentration was not enough to inhibit the whole surface, whereas MEG efficiency was able to inhibit the surface by 80.48%.
- The time of exposure and the surface that will be protected, much be considered to make a choice of inhibitor to gain a higher possible of the efficiency.
- There was no synergic effect between WMSE and MEG related to the mixture efficiency that was lower than MEG efficiency.

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