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A Corrosion Inhibition through the Adsorption of Cacao (Theobroma cacao) Peels Extract on Steel Surfaces: Experimental and DFT Results

Apriska Prameswari[1], Dahyunir Dahlan[1], Yuli Yetri[3,*], Imelda Imelda[2]

[1] Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Andalas, Padang 25613, Indonesia
[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Andalas, Padang 25163, Indonesia
[3]Padang State Polytechnic, Padang 25613, Indonesia

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Corresponding Author:
Yuli Yetri
Email: yuliyetri@pnp.ac.id

ABSTRACT

Steel surface coating has been carried out using the immersion method in an inhibitor of cacao (Theobroma cacao) peel extract for 24, 72, 120, and 168 hours. The corrosion treatment was performed using HCl with different immersion time of 48, 96, and 144 hours after coating process with the inhibitor. Corrosion testing with the weight loss method gave the best results with the lowest corrosion rate of 0.2972 mg.cm^2/hour and inhibition efficiency of 74.7128% for steel samples with the longest immersion time in inhibitor. Optical microscopy and SEM images indicated that the longer the immersion time in the inhibitor, the better (i.e., fewer holes and cracks) the surface morphology of the steel. The appearance of four sharp peaks in the XRD diffractogram indicated that the samples with the lowest corrosion rate produced Fe and C crystalline phases due to the reaction between the steel surface and the inhibitor. A quantum chemical analysis using the DFT (Density Functional Theory) method also produced a fairly high inhibition efficiency and was close to the experimental results of 80.2098%.

1. INTRODUCTION

Industries nowadays have grown so rapidly that cause increasing utillizations of various metals, such as iron, steel, aluminum, and others. Many factors cause the decreasing efficiency of metals, one of which is the corrosion or rusting of metals. Metal rusting occurs due to the reaction of the metal with the environment which then reduces the quality of the metal itself and results in the short service life of the metal (Dariva & Galio, 2014; Yetri et al., 2020a). One of the protection and control measures to minimize metal deterioration is by giving organic inhibitors, such as cacao peel extract (Theobroma cacao) (Yetri et al., 2020b). Inhibitor addition becomes one of the most effective methods to control corrosion because it is more efficient, effective, and environmental-friendly. The application of corrosion inhibitors is quite easy, thereby has been widely applied in industries (Yetri & Jamarun, 2016, 2017). Cacao is one of the plantation products that produce a massive amount of waste in the form of peels, namely around 75% of the total weight of produced cacao. Cacao peel contains tannin compounds that can form complex compounds with Fe (III) on the metal surface that will block the attack of corrosive ions on the metal surface (Tissos et al., 2018). The corrosion inhibition study of mild steel in 1.5 M HCL and NaCl media using cacao peel extract has been carried out by Yetri et al. using weight loss method and electrochemical measurement (Yetri & Jamarun, 2017; Yetri et al., 2020a).

Yetri et al. (2017) show that the efficiency of inhibition increases with increasing concentration of cocoa peel extract. This study conducts a steel surface coating using an organic inhibitor of cacao (Theobroma cacao) peel on steels with HCl as the corrosive medium. The method used was immersion, where the steel surface was immersed into the obtained cacao peel extract. Immersion time in the inhibitor was varied to determine the adsorption ability of the cocoa peel extract inhibitor on the steel surface, while the weight loss method was used to see the corrosion process that occurs.

2. METHODS

2.1 Preparation of Steel sample and Cacao Peel Extract Inhibitor

Steel with a length of 2 cm, a width of 1 cm, and a height of 3.5 g was polished with sandpaper to smooth the surface. After polishing, the steel was washed using aquadest to remove dirt, grease, and rust adhering to the steel. After that, the steel was allowed to stand for one day and put into a sample container. Cacao peels were first separated from the fruit, then thinly sliced and dried at room temperature for approximately 14 days. After drying, the cacao peels were crushed with a blender, then macerated using 70% ethanol for 3 days. The macerated cacao peels were filtered and concentrated using a rotary vacuum evaporator to obtain a concentrated extract of the cacao peels.

2.2 Steel Surface Coating in Cacao Peel Extract Inhibitor

The clean steel was then coated or soaked with a concentrated cacao peel extract for 24, 72, 120, and 168 hours to allow the inhibitor from the cacao peel extract permeated the steel surface. After immersion with inhibitors with varying duration, the steel was removed from the container containing the cacao peels, allowed to stand for one minute and continued with immersion in 1.5 M HCl for 48, 96, and 144 hours to see the effect of corrosion on the steel surface.

2.3 Determination of the Corrosion Rate using the Weight Loss Method

The corrosion rate was calculated from the weight reduction per unit time per unit area. The weight loss method is considered one of the most authentic methods in determining the corrosion rate for corrosion-free conditions. The principle of the weight loss method is calculating the amount of material lost after the immersion test in corrosive media is carried out. The flow chart of the process of determining the corrosion rate using the weight loss method can be seen in Figure 1.

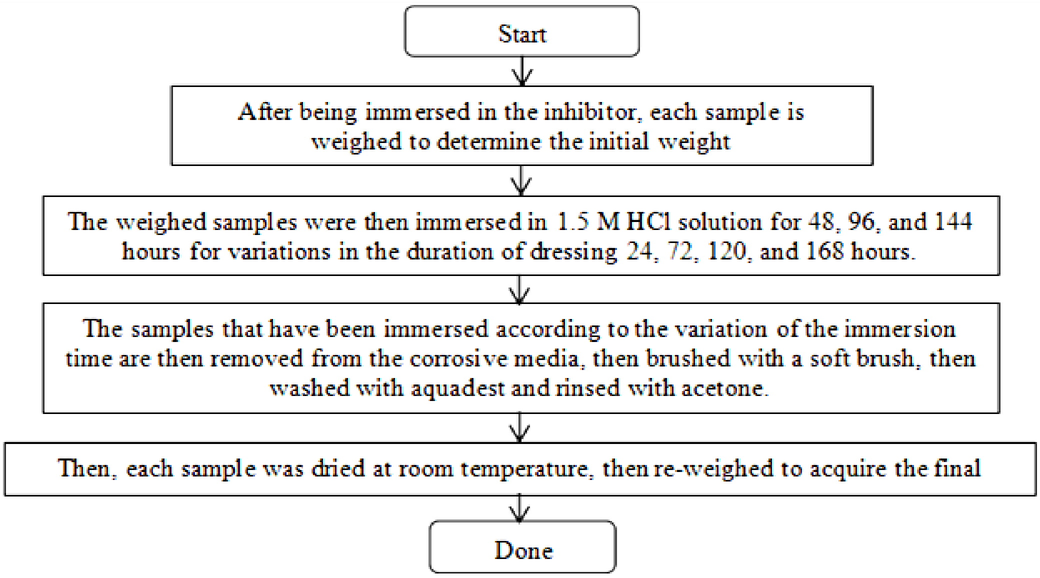


Figure 1. The flow chart of the process of determining the corrosion rate using the weight loss method

The equation of corrosion rate with weight loss and inhibition efficiency methods (% IE) are given in Equation (1) and Equation (2):

$$V = \frac{\Delta m}{A\ t} \quad (1)$$

$$\%\ \mathrm{EI} = \frac{V_0 - V_1}{V_0}\ \mathrm{X}\ 100\% \quad (2)$$

V is the corrosion rate of steel (gr/cm^2.hour), Δm is weight loss (grams), A is cross-sectional area (cm^2), and t is time (hours). The inhibitor performance parameter is expressed as *% EI* where V_0 is the corrosion rate without inhibitor and V_1 is the corrosion rate after the addition of the inhibitor.

2.4 Sample Characterizations

The characterization of the steel coating with cacao peel extract inhibitor was performed using XRD, SEM, optical microscopy, and quantum chemistry. XRD was conducted to determine the type and size of the crystals formed in the samples (Tarapitakcheevin et al., 2013; Mahaputri et al., 2018). Optical microscopy and SEM were performed to see the surface morphology of steel that had been coated with the inhibitor and given corrosion treatment. Quantum chemical analysis was done to determine the efficiency of iron corrosion inhibition of tannin molecules experimentally (El Hosary et al., 1972; Gece, 2008). The tannin molecule was optimized using a Gaussian 16W program package with the DFT calculation method and the B3LYP/6-31G basis set (Hasan & Edrah, 2011; Ananta et al., 2015). The corrosion efficiency value of the tannin compound can be predicted using Equations (3), (4), and (5):

$$\mathrm{I_{add}}\% = \frac{\mathrm{I_{inh}} - \mathrm{I_{x-inh}}}{\mathrm{I_{inh}}}\ \mathrm{x}\ 100\% \quad (3)$$

$$\mathrm{EI_{add}}\% = \mathrm{I_{add}}\%\ \mathrm{x}\ \mathrm{EI_{eksp}}\% \quad (4)$$

$$\mathrm{EI_{teori}}\% = \mathrm{EI_{add}}\% + \mathrm{EI_{eksp}}\% \quad (5)$$

$\mathrm{I_{add}}$% is the percentage of potential ionization of the tannin compound, $\mathrm{I_{inh}}$ is the ionization potential of the parent compound (tannin), $\mathrm{I_{x\text{-}inh}}$ is the ionization potential of the Fe-inhibitor, $\mathrm{EI_{add}}$% is the percentage of corrosion inhibitory efficiency of the tannin inhibitor compound, $\mathrm{EI_{eksp}}$% is the percentage of the corrosion inhibitory efficiency of the corrosion inhibitor from the experimental results, $\mathrm{EI_{theory}}$% is the theoretical corrosion inhibitor efficiency.

3. RESULTS AND DISCUSSION

3.1 The Effect of Immersion Time of Steel in Inhibitor and HCl on Steel Mass Loss

Variations in the addition of immersion time in HCl affect the mass loss of steel. In each variation of the immersion time in the inhibitor, there were 3 variations of the immersion time in HCl which increased over time, causing the steel mass loss to increase. It can be seen that the steel immersed in the inhibitor for 24 hours produces in the smallest weight loss of 88.3 mg when immersed in HCl for 48 hours and the largest 388.2 mg when immersed in HCl for 144 hours. Figure 2 shows that the duration of immersion in HCl is directly proportional to the mass loss of steel. The variation of immersion time with increasing HCl will result in an increase in mass loss. This occurs due to the ability of HCl which tends to aggressively erode the steel surface and make the surrounding environment corrosive (Abboud et al., 2016). Figure 2 shows the measurement results between immersion time in HCl and steel mass loss.

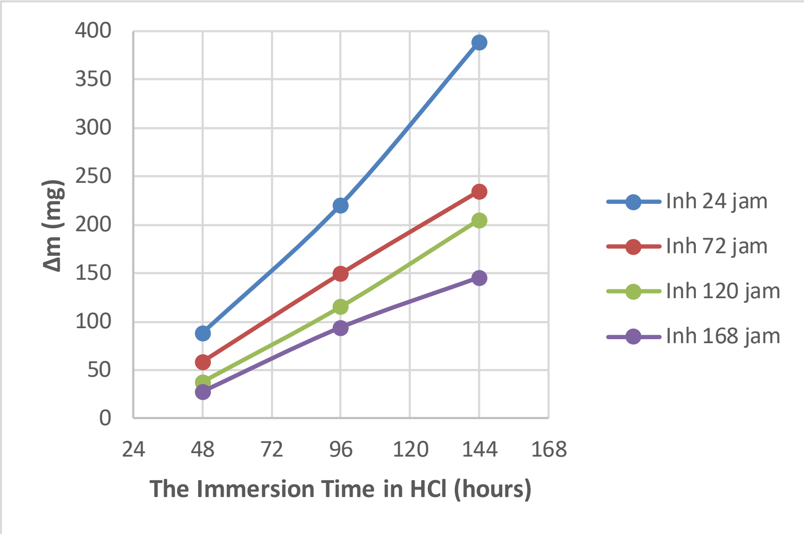


Figure 2. The effect of immersion time in HCl on steel mass loss

3.2 The Effect of Immersion Time of Steel in Inhibitor and HCl on Steel Corrosion Rate

The sample with the highest corrosion rate was the sample immersed in inhibitor for 24 hours and HCl for 144 hours, with a corrosion rate of 1.3479 mg/cm^2.hour. The sample with the longest immersion time in the inhibitor and the shortest HCl was the most optimal sample with the lowest corrosion rate of 0.2972 mg/cm^2.hour in which this sample was immersed in the inhibitor for 168 hours and HCl for 48 hours. The cacao peel extract inhibitor given with the addition of immersion time will cause the corrosion rate on the steel surface to decrease. This occurs because the longer the immersion of the steel in the cacao peel extract, the more the amount of adsorbed inhibitor will be. Therefore, the tannin compound present in the cacao peel extract will form more complex compounds with Fe (III), so that a thicker protective layer will be formed on the steel surface.

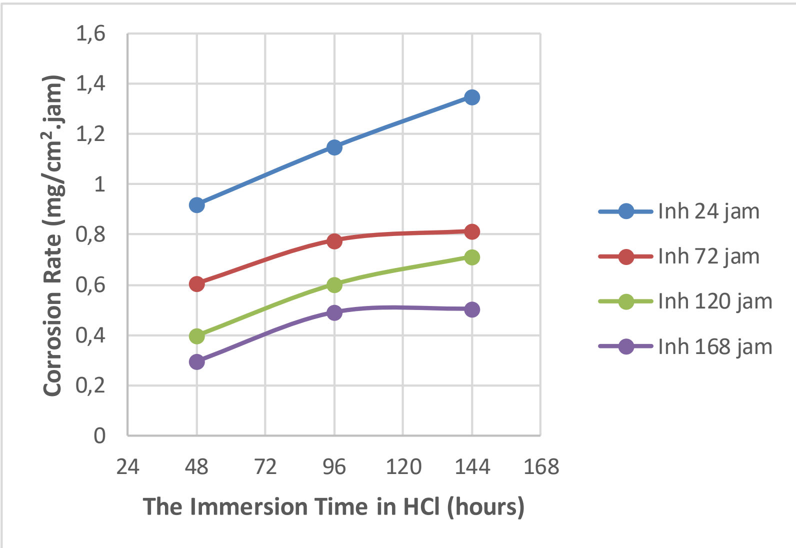


Figure 3. The effect of immersion time in HCl on steel corrosion rate

The effect of immersion time in inhibitor and HCl on the corrosion rate of steel is shown in Figure 3. The HCl corrosive medium significantly changes the corrosion rate of steel. This can be seen from the decreasing graph for each variation of the addition of immersion time in HCl. Increasing the immersion time of steel in HCl results in a higher surface erosion process, this due to HCl being a strong acid and having high corrosive properties (Ostovari et al., 2009).

3.3 The Effect of Immersion Time of Steel in Inhibitor and HCl on Inhibition Efficiency

The sample with 24 hours immersion in inhibitor and 144 hours in HCl produces an inhibition efficiency of 6.4543%, while the sample with 168 hours immersion in inhibitor and 48 hours of HCl is the sample with the highest inhibition efficiency which is around 75% (Fig. 4). This inhibition efficiency value is obtained based on the corrosion rate that occurs on the steel surface after being immersed in HCl corrosive media for 48, 96, and 144 hours. It can be seen that the inhibition efficiency value is inversely proportional to the corrosion rate value, where the smaller the corrosion rate, the higher the inhibition efficiency (Setiawan et al., 2017). HCl used as a corrosion medium has proven that immersion of steel for a short time prevents the formation of tannin-iron complexes, therefore, the corrosion rate will be higher and the efficiency lower. This inhibition efficiency indicates the ability of the cocoa peel extract inhibitor to inhibit the corrosion process.

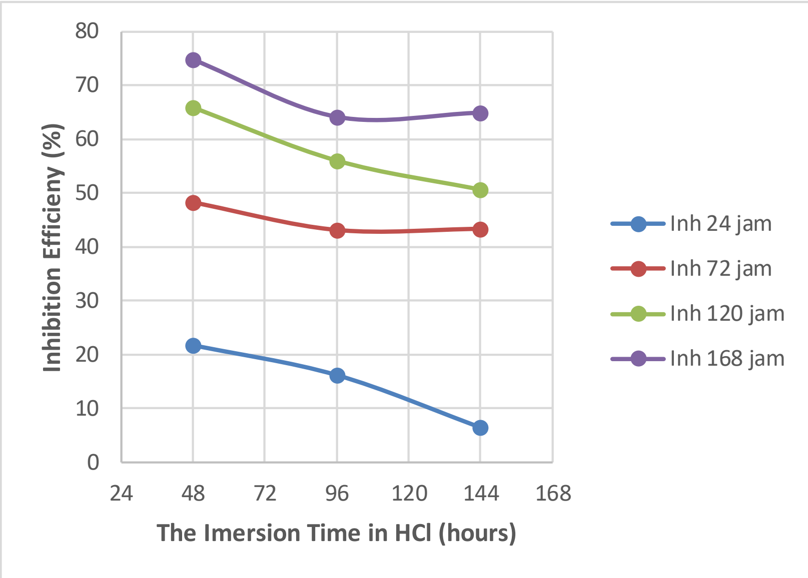


Figure 4. The effect of immersion time in HCl on inhibition efficiency of steel corrosion

3.4 Optical microscope images of steel samples

Figure 5(a) is the sample without inhibitor and has not subjected to corrosion, it can be seen that the sample surface is filled with remnants of the polishing process, no lumps or corrosion arise because this sample has not reacted with oxygen and acidic media. The samples in Figures 5(b) to 5(d) (immersion in inhibitor for 24 hours, HCl for 48, 96, and 144 hours) show that the coating has not yet formed so scratches from sanding and corrosion are visible. The steel samples in Figures 5(e) to 5(g) (immersion in inhibitor for 72 hours, HCl for 48, 96, and 144 hours) have indicated a layer formed since the morphology of the polished steel is no longer visible. The most optimal sample can be observed in Figure 5(k) where the surface morphology obtained is more evenly distributed compared to other sample, and the corrosion that occurs is also the least. This is the result of the longest time the sample was immersed in cacao peel extract was 168 hours, while the corrosion treatment given was the smallest time variation.

3.5 *Scanning Electron Microscope* images of steel samples

The effect of immersion time in cacao peel extract and HCl on the surface morphology of steel can be observed SEM images. Figure 6(a) shows that the sample has a lot of damage in the form of very large holes, lumps, and cracks indicating that very high corrosion has occurred. This sample was immersed in cocoa peel extract for a very short time and in HCl for the longest time.

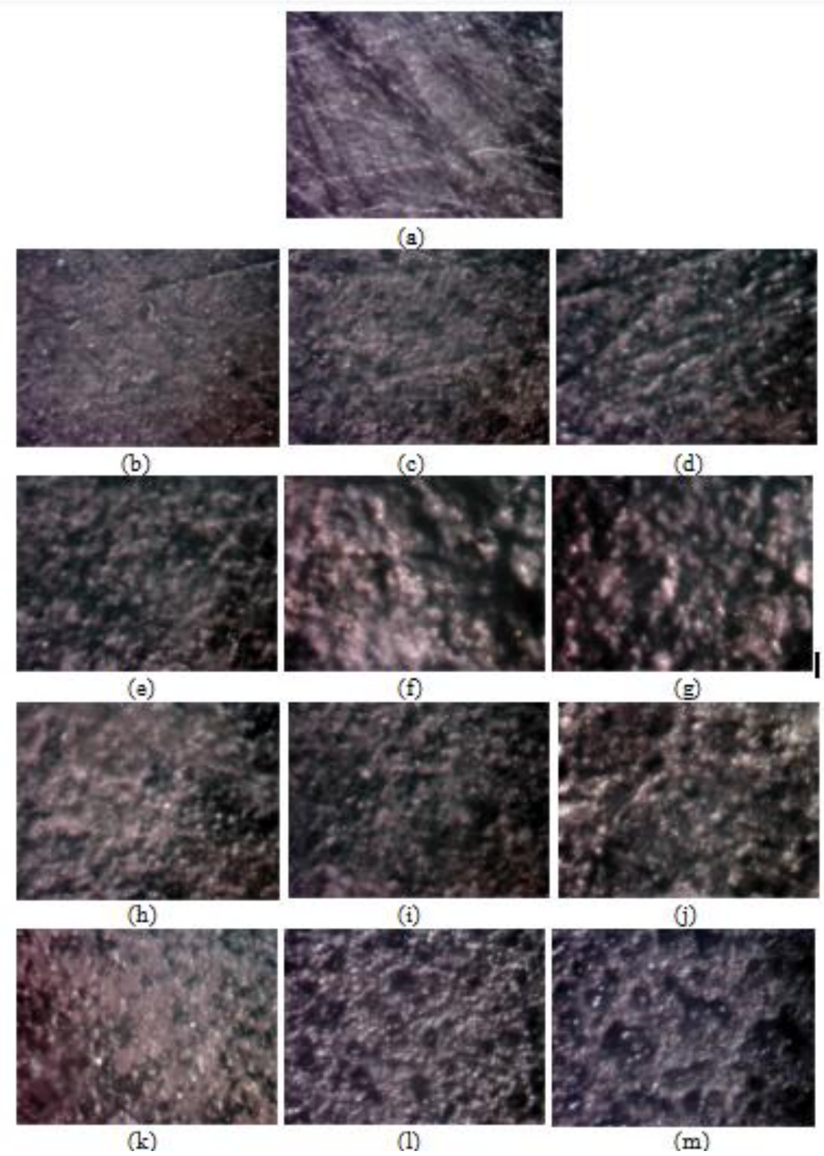
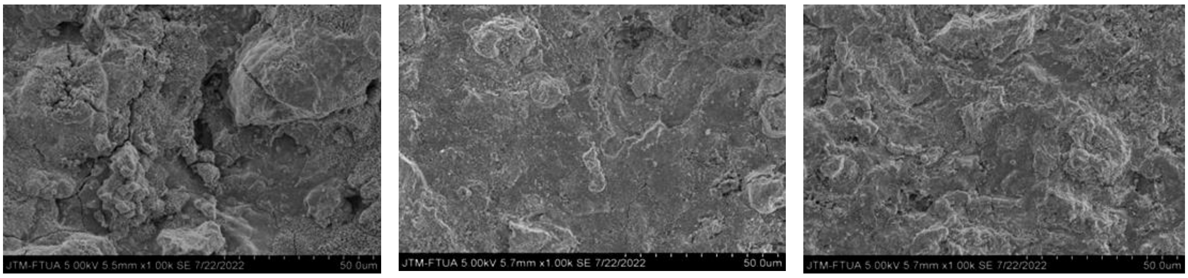


Figure 5. The morphology of steel sample surface, (a) without inhibitor, (b) 24 h inhibitor and 48 h HCl, (c) 24 h inhinbitor and 96 h HCl, (d) 24 h inhibitor and 144 h HCl, (e) 72 h inhibitor and 48 h HCl, (f) 72 h inhibitor and 96 h HCl (g) 72 h inhibitor and 144 h HCl, (h) 120 h inhibitor and 48 h HCl, (i)120 h inhibitor and 96 h HCl, (j) 120 h inhibitor and 144 h HCl, (k) 168 h inhibitor and 48 h HCl, (l) 168 h inhibitor and 96 h HCl, and (m) 168 h inhibitor and 144 h HCl

The surface morphology of the sample in Figure 6(b) is much more refined than that of the sample in Figure 6(a). It appears that the steel surface is thicker and flatter, although there are still cracks and irregularities due to immersion in HCl. The steel surface The steel surface morphology results in Figure 6(c) show that this sample has a rougher surface and more pits than the sample in Figure 6(b), but better than the sample in Figure 6(a). A longer soaking time will make the interaction between polyphenolic tannins and iron compounds stronger (Favre & Landolt, 1993). The interaction makes more tannin compounds adsorbed to the steel surface, thus forming complex compounds with Fe(III) that will protect the steel surface from corrosion damage.



(a) (b) (c)

Figure 6. The SEM images for samples (a) 24 h inhibitor and 144 h HCl, (b) 168 h inhibitor and 24 h HCl, and (c) 168 h inhibitor and 144 h HCl

3.6 *X-Ray Difraction (XRD) diffractogram*

The result of XRD characterization in Figure 7(a) shows that the sample with the highest corrosion rate contains magnetite (Fe_3O_4) phase as an excessive corrosion product. The magnetite phase is formed due to the interaction between Fe and OH^- (Rani & Basu, 2012). The XRD results in Figures 7(b) and 7(c) shows that the XRD test results for the two samples each produced four sharp peaks indicating the formation of a crystalline phase. The second XRD produced Fe and C phases, while the samples with the longest variation of immersion time in inhibitor and HCl had four peaks with the same phase, namely Fe. This indicated that the sample still contains a lot of Fe.

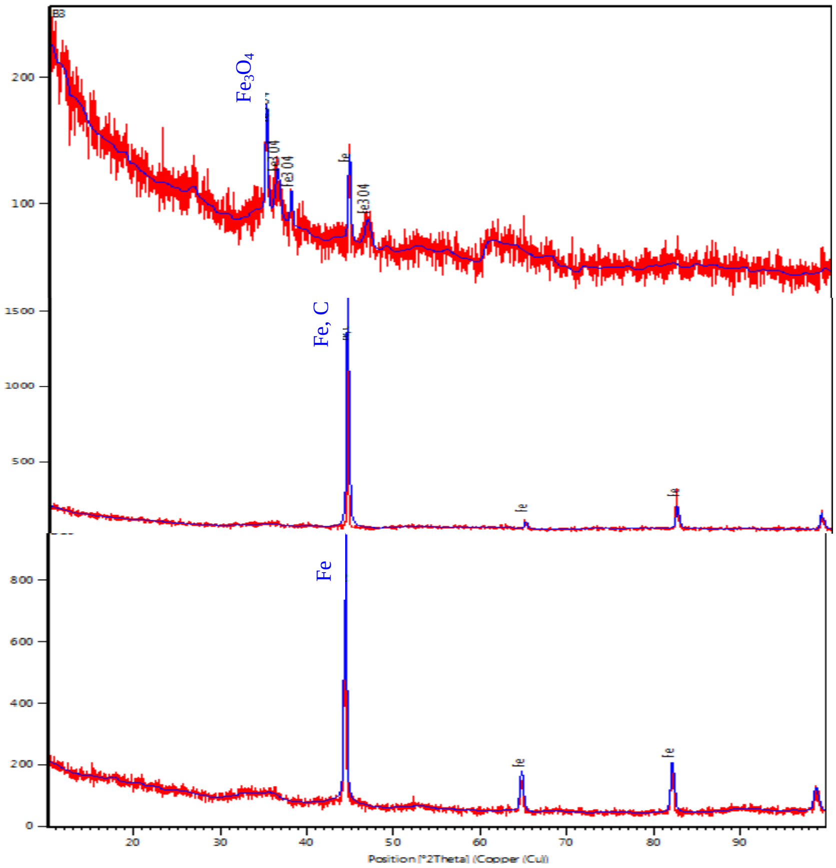


Figure 7. The XRD results for samples immersed in inhibitor for 24 hours and HCl for 144 hours, inhibitor for 168 hours and HCl for 48 hours, and inhibitor for 168 hours and HCl for 144 hours.

3.7 Quantum Analysis

A corrosion inhibitor is a compound that can inhibit the corrosion in metals, one of the corrosion inhibitor compounds is tannin. Tannin compound can be used as an inhibitor as it has free electron pairs and π electrons in its molecular structure (Hsissou et al., 2020). Figure 8 and Figure 9 show the molecular structure, optimal geometric structure, HOMO and LUMO contours for the optimized pure tannin and tannin-Fe compounds. The HOMO and LUMO contours can predict the absorption center and the interaction of inhibitor molecules. The HOMO contour shows the electron donor region while the LUMO contour shows the electron acceptor region (Fu et al., 2010). It can be seen in Figure 8 that the HOMO contour is centered on the bond and the oxygen atom in the cyclic chain B and LUMO is centered on the C atom, this indicates that the OH group in the B chain can function as an electron donor to Fe, while in Figure 9, it can be seen that the HOMO and LUMO contours are centered on groups bonded to Fe atoms, this explains that there is a good electron donor and transfer between tannins and Fe.

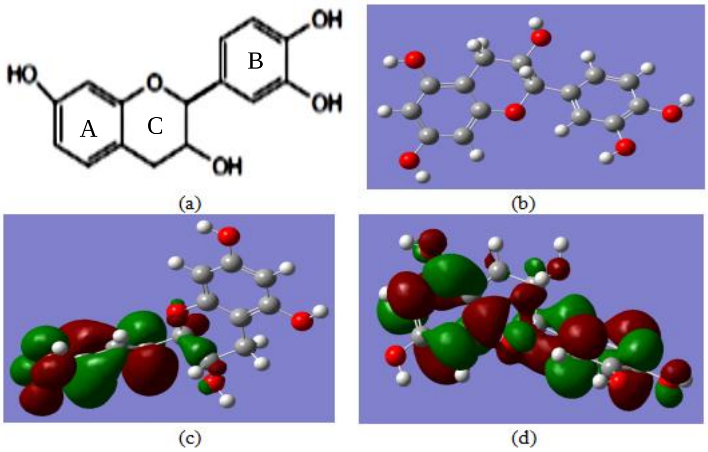


Figure 8. The optimization results of tannin compound, (a) molecular structure, (b) optimal geometric structure, (c) HOMO contour, and (d) LUMO contour

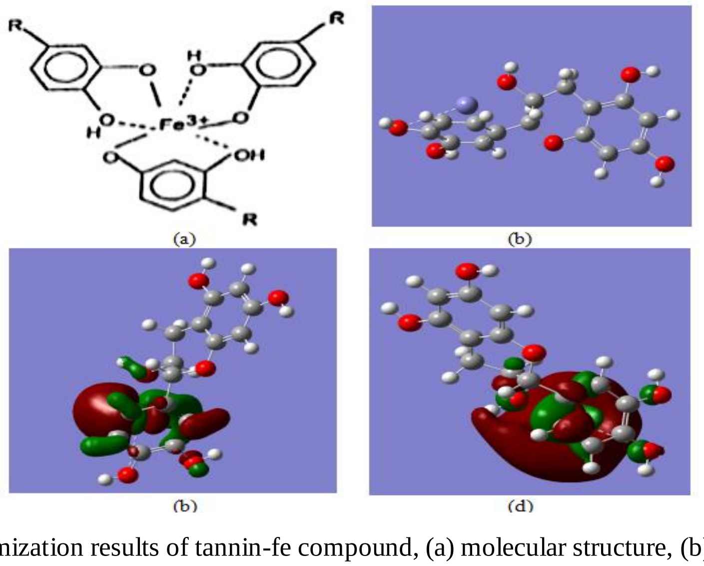


Figure 9. The optimization results of tannin-fe compound, (a) molecular structure, (b) optimal geometric structure, (c) HOMO contour, and (d) LUMO contour

Table 1. Quantum Chemical Parameters

Pure Tannin		**Tannin + Fe**		**I_{inh} (eV)**	**$I_{x\text{-}inh}$ (eV)**	**EI_{theory} (%)**
E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	2.9998	2.7949	80.2098
-2.9998	-1.3996	-2.7949	-0.9222			

Table 1 shows the quantum parameter values acquired from the optimization using Gaussian 16W program and DFT method for pure tannin and tannin-Fe compounds. The corrosion inhibition efficiency (IE theory%) of tannin compounds was calculated using the DFT-B3LYP/6-31G method. Quantum chemical calculations resulted in a high tannin compound inhibition efficiency of 80.2098%, while the maximum inhibition efficiency obtained in this experiment was 74.7128%. This proved that the experimental and theoretical results are in agreement, which means that the tannin compound has a good ability to reduce or inhibit the corrosion rate of steel by forming complex compounds with iron so that the steel surface will be covered and protected from corrosion attacks. The E_{HOMO} and E_{LUMO} values (Table 1) of the Fe-tannin complex also changed compared to pure tannin, this indicated that Fe orbitals have been combined with tannins.

4. CONCLUSION

Based on the study, testing, and analysis that had been done, it can be concluded that the tannin compounds contained in the cocoa (Theobroma cacao) peels have a fairly high efficiency, namely 74.7% (weight loss method) and 80.2% (DFT method) in inhibiting the corrosion rate of steel. This can be provenby the decreasing value of the corrosion rate when the immersion time in the given inhibitor that has been given is getting longer. The results of XRD characterization, optical microscopy, SEM and quantum chemical calculations have also shown that cocoa peels are able to reduce the corrosion rate of steel by forming complex compounds with iron so as to protect the steel surface from corrosion.

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