

Characterisation of Adsorption Inhibitors of Cacao Peel Extract to Protect the Rate of Corrosion on Steel Surfaces

**Yuli Yetri^{1*}, Dahyunir Dahlan², Rakiman¹, Maimuzar¹,
and Wan Mohd Norsani Wan Nik³**

¹Mechanical Engineering Department,
Politeknik Negeri Padang,
Padang, 25163, Indonesia.

²Department of Physics, Faculty of Mathematics and Natural Sciences,
Universitas Andalas, Padang, 25173, Indonesia.

³Maritime Technology Department, Faculty of Ocean Engineering Technology,
Universiti Malaysia Terengganu,
21030 Kuala Nerus, Terengganu, Malaysia.

*Corresponding Author's Email: yuliyetri@pnp.ac.id

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Abstract

Research has been conducted to investigate the use of biomass waste inhibitors derived from cocoa pod extract to reduce steel corrosion rates. Steel samples were pre-soaked in the inhibitor for 24, 72, 120, and 168 hours, followed by immersion in a corrosive HCl medium for 48, 96, and 144 hours. The corrosion rate was evaluated using the weight loss method, optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Additionally, X-ray diffraction (XRD) phase analysis and Density Functional Theory (DFT) were employed to examine the HOMO/LUMO contours, molecular geometry, and structure. The weight loss method yielded the best results, with the lowest corrosion rate of 0.2972 mg/cm²/hour and inhibition efficiency of 74.71%, observed when the steel was soaked in the inhibitor for 168 hours and immersed in HCl for 48 hours. Morphological analysis using optical microscopy and SEM revealed that longer immersion in the inhibitor resulted in a smoother surface with fewer cracks. XRD analysis identified four distinct peaks corresponding to crystalline Fe and C phases, indicating reactions between the steel surface and the inhibitor. AFM analysis demonstrated a strong correlation between the duration of immersion in the inhibitor and the extent of adsorption on the steel surface. The DFT analysis showed that a molecule's corrosion inhibition potential increases with higher EHOMO values, as this facilitates electron transfer to the steel surface. The optimization and computational analysis of tannin components interacting with the steel surface revealed a high inhibition efficiency of 80.21% for the cocoa pod extract inhibitor, suggesting its potential as an effective and sustainable solution for industrial corrosion control. These findings highlight the need for further optimization and scalability studies, with implications for the widespread use of natural inhibitors in various corrosive environments.

Keywords: Adsorption, Cocoa Skin, Steel Corrosion, Eco-friendly Inhibitors, Density Functional Theory

1.0 Introduction

Because steel is strong, pliable, readily oxidised, and has superior electrical and thermal conductivity, it is widely used in many different sectors and

utilities, including building materials, home appliances, and car frames [1]. However, one of steel's drawbacks is its tendency to rust quickly, which diminishes its mechanical properties. This rusting occurs due to a chemical reaction between the metal and the environment, which can compromise its quality and shorten its service life [2].

It must be prevented because corrosion is harmful and can lead to several issues. The addition of inhibitors is one of the many methods that have been tried to slow down the pace of corrosion. The industrial world frequently uses inhibitors because they are inexpensive, effective, and straightforward. As a result, they are one of the most efficient ways to prevent corrosion [3]. Because they are more accessible, affordable, eco-friendly, and non-toxic than inorganic inhibitors, organic inhibitors are utilised more frequently for this reason [4].

Steel corrosion can be slowed down by using plant extracts made from plant parts, including leaves, bark, roots, fruits, and stems that include organic components such as tannins, alkaloids, saponins, acids of amino, and proteins [5]. One could argue that organic inhibitors are crucial to corrosion prevention tactics. The cocoa skin (*Theobroma cacao*) is one plant with a high tannin content [6]. Approximately 75% of cocoa pods are wasted in the shell. This cocoa pod has not been exploited to its full potential and is frequently thrown away, harming the ecosystem. Tannins found in cacao skin can react with Fe (III) to create complex compounds that impede the entry of corrosive ions onto metal surfaces [7].

Using weight loss and electrochemical measuring techniques, Yetri et al. [5] investigated the potency of cocoa skin extract as an inhibitor against mild steel in a 1.5 M HCl and NaCl environment. The results showed that as the content of cocoa pod extract grew, so did the inhibitory efficiency. According to [1], [3], and [8], the best inhibition efficiency for each inhibitor at a 2.5% v/v concentration in HCl and NaCl 1.5M is 96.26% (weight loss), 92.68% (Tafel), 95.64% (Rp), 85.78% (EIS), and 91.93% (weight loss), 85.90% (Tafel), 90.19% (Rp), and 75.23% (EIS) over 768 hours.

Furthermore, the study [5] used the weight loss and Tafel method in combination with crude extracts and polar extracts of cacao peels to prevent steel corrosion rate in a 1.5 M corrosive solution, including hydrochloric acid. The inhibition efficiency measurement is conducted over 192 hours at a 303-323 K temperature range, with extract concentrations ranging from 0.5-2.5% at 0.5% intervals. At 30 °C (303 K), the optimal conditions are attained at doses of 2.5% inhibitor. On the other hand, the corresponding inhibitory efficiencies of polar extract and crude extract are 83.45% and 96.26% for weight loss, 85.23% and 92.08% for Tafel, and 72.29% and 83.95% for EIS.

To determine how successfully the corrosion inhibitor in the cocoa pod extract adsorbs to the steel surface and limits the corrosion rate, the steel is first immersed in the mixture for varied amounts of time. To enable the cocoa pod extract to adsorb on the surface, immerse the object in the extract. After this,

it was put in a hydrochloric acid-containing 1.5 M corrosive medium. Steel samples were immersed in the inhibitor for varied lengths in this study. However, in earlier studies, inhibitors were added to the corrosive medium by changing the inhibitor's concentration [3].

2.0 Research Methodology

This work was conducted at the Department of Physics, Laboratory of Materials Physics, Andalas University, Padang, to determine the corrosion rate utilising a weight loss technique. Padang State University conducted XRD characterisation. The Material Physics Laboratory, Andalas University Mechanical Engineering Laboratory, Unsyiah Mechanical Engineering Laboratory, and SEM Mechanical Engineering Laboratory investigated surface morphology using optical microscopy and DFT for quantum chemistry.

For this investigation, the following supplies and equipment were required: cocoa pods, 1.5 M hydrochloric acid (HCl), steel plates, distilled water, ethanol, acetone, filter paper, sandpaper, aluminium foil, beaker, magnetic stirrer with hot plates, digital scales, rotary vacuum evaporators, grinding machines, measuring cups, spatulas, glass containers, Erlenmeyer flasks, laptops, and steel plates.

2.1 Research Procedure

The work procedures for preparing fruit peel abstracts and steel surface preparation follow those carried out in previous research [1], [3]. Meanwhile, the characterisation includes Optical Microscope, XRD, SEM, AFM, and DFT. Compiling the materials and analysing the findings marked the beginning and finish of the working procedure for this investigation.

2.2 Material Preparation

The manufacturing of the cocoa pod extract and the grinding and cleaning of the steel surface were done following the methodology employed by [3], the previous researcher. After the concentrated cocoa pod extract was obtained, the steel was soaked in the extract for 24, 72, 120, and 168 hours, depending on the technique. After the immersion time was up, the steel was immersed in 1.5 M HCl for 144 hours.

3.0 Results and Discussion

Table 1 shows the effect of immersion length in cocoa pod extract on mass loss and steel corrosion rate. The time the cocoa pod extract is soaked determines the mass change of steel formed. The extended immersion time in the inhibitor causes the cocoa pod extract to get more adsorbed on the steel surface. The mass of the steel rose by 232.37 mg, or 0.23 grams, after 168 hours and by 89.57 mg, or 0.0896 grams, after 24 hours of immersion. This suggests that the rise in mass is precisely related to the growth in immersion duration.

A complex material (thin layer) developed on the steel's surface throughout the inhibitor's prolonged immersion length due to increasing interaction between the tannin molecules in cocoa pod extract and iron (Figure 1). The thin layer thickened due to the extended immersion duration, giving HCl more opportunity to degrade the steel surface. Consequently, the corrosion and mass loss rate due to surface erosion decreased [9], [10].

Once the steel sample is submerged in the corrosive medium HCl, the corrosion rate and inhibition efficiency are determined using the weight loss method. Table 1 displays the computation results produced by applying equations (1) and (2).

$$V = \Delta m / \Delta \quad (1)$$

where V is the steel corrosion rate (gr/cm².hour), Δm is weight loss (grams), A is the cross-sectional area (cm²), and t, is time (hours).

$$\%EI = \frac{(V_o - V_i)}{V_o} \times 100\% \quad (2)$$

where Vo is the corrosion rate without the inhibitor, and V1 is the corrosion rate after adding the inhibitor.

Table 1: Corrosion rate, mass loss, and inhibition efficiency as a function of inhibitor immersion time

No	Variable	Inhibitor Immersion Time (hours)			
		24	72	120	168
1	Corrosion Rate (V)	1.1389	0.7340	0.5711	0.4317
2	Inhibition Efficiency (IE)	14.7916	44,9568	57,5620	74.7128

Table 1 depicts how the corrosion rate drops as the immersion period in the cocoa shell extract inhibitor increases. It is more difficult to be harmed by corrosive media because of the layer of cocoa pod extract that forms on the surface, which thickens and increases the adsorption capacity. As a result, the cocoa pod extract's tannin components will combine with Fe (III) to generate more complex compounds, thickening the protective layer on the steel surface. Another significant factor influencing the inhibitor's effectiveness is the duration of immersion [11]. This is because the efficacy of inhibition suggests that the cocoa pod extract has corrosion-inhibiting qualities [12].

The better the inhibition efficacy, the longer it is submerged in the inhibitor. Table 1 shows an inverse relationship between inhibition efficiency and corrosion rate, with inhibition efficiency rising as the corrosion rate falls. After 168 hours of immersion in the inhibitor, the maximum efficiency of the inhibition value averages 74, 7128%. This indicates that the adsorption of cocoa pod extract on steel's surface can create a protective layer that prevents corrosion attack [13].

3.1 Surface Morphology Analysis

The optical microscope Bright-field iScope IS.1153-EPL, SEM Hitachi Type: TM3000 and AFM A62.450 were used to perform characterisation analysis on the steel surface. As demonstrated in Figure 1, all samples were first examined under an optical microscope after being submerged in the corrosive medium HCl 1.5 M for varying lengths of 24, 72, 120, and 168 hours.

The results of optical microscopy studies of the steel surface morphology with and without additional inhibitors, such as a 1.5 M HCl corrosion solution, are shown in Figure 1. Because the surface of untreated steel has not been tainted with oxygen, Figure 1a shows its flawless appearance. The surface of Figure 1b, submerged in a corrosive liquid without an inhibitor, is rough and degraded by corrosion. The corrosion on the steel's surface morphology is seen in Figures 1c to 1f immersion in 1.5M HCl with different inhibitors for 24, 72, 120, and 168 hours. The corrosion thins out as the inhibitor immersion period increases.

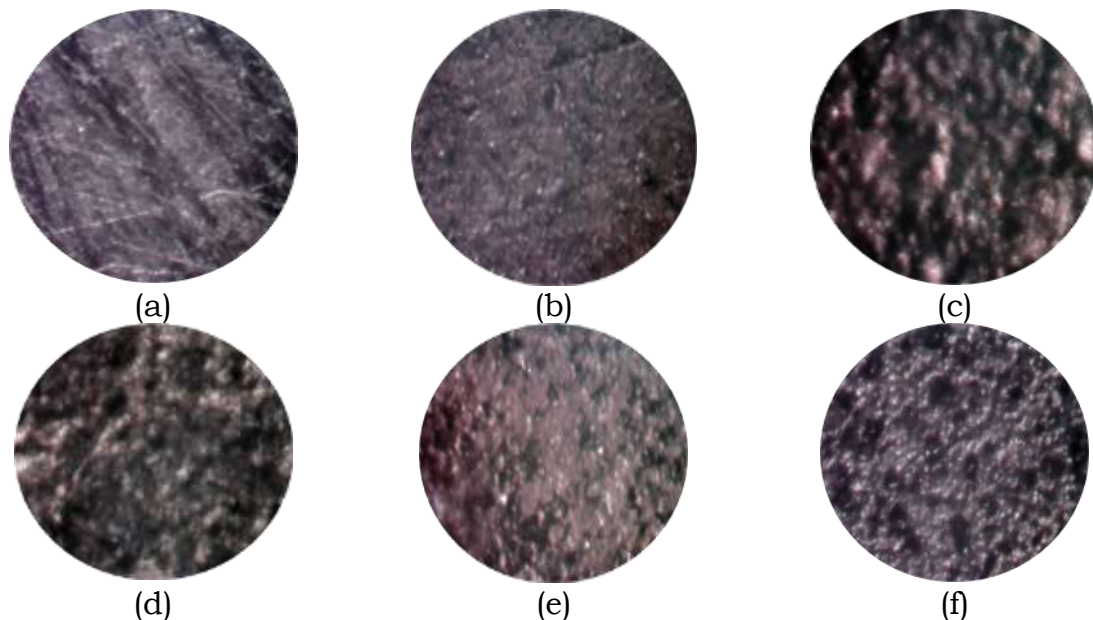


Figure 1: Steel surface morphology using an optical microscope in 1.5 M HCL medium for 144 hours with variations in immersion time in inhibitors with 100X magnification (a) without treatment (b) without inhibitors (c) 24 hours (d) 72 hours (e) 120 hours and (f) 168 hours

This illustrates that the more cocoa pod extract is absorbed onto the steel surface, the slower the corrosion rate is. According to earlier studies, the corrosion rate decreases when there is more significant adsorption of cocoa pod extract on the steel surface [8]. This has been verified by [1], using EDX analysis, which demonstrates that C and O levels rise following adsorption on the steel surface.

The SEM with a 1000x magnification was also used to characterise the steel's surface morphology (Figure 2). After being submerged in an inhibitor for 168

hours in HCl for 144 hours, the sample with the lowest corrosion rate is shown in Figure 2e. The adsorption of cocoa pod extract on the steel surface increases with the time it is submerged in the inhibitor, as seen in Figure 2. According to the findings of the EDX test, [14] demonstrates that the corrosion rate decreases with increasing surface adsorption. For the metal and its components to be shielded from the corrosion rate by the adsorption in the form of a layer. The photos in Figure 2(e) above demonstrate that the longer the immersion time in the inhibitor, the smoother the completed surface is, as the corrosion rate and the damage caused by corrosion decrease. The resulting layer is more uniform and has a lot of adsorptions on its surface, but it still has bubbles and cracks from the immersion in HCl. This illustrates how the shape of the steel surface varies as immersion duration increases. According to [15], longer soaking time results in more interactions between the tannin polyphenolic compounds and iron and increased tannin adsorption onto the steel surface. This complex formation with Fe (III) protects the steel surface from corrosion attack.

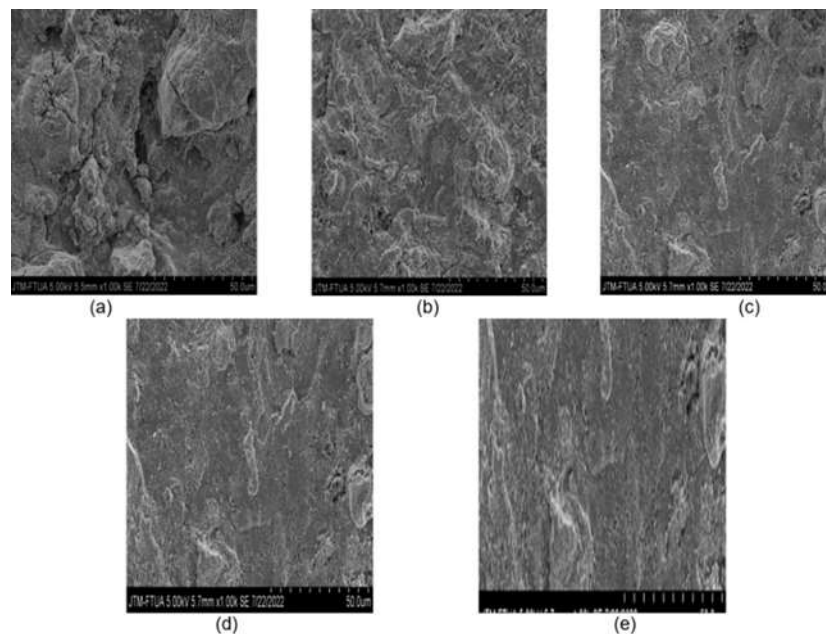


Figure 2: Morphology of steel surfaces by SEM in 1.5 M HCl medium for 144 hours with variations in immersion time in inhibitors with 1000X magnification (a) without Inhibitors, (b) 24 hours, (c) 72 hours, (d) 120 hours, and (e) 168 hours

3.2 X-Ray Diffraction Analysis

Samples with the highest and lowest corrosion rates in 1.5 M HCl were characterised using X-ray diffraction (XRD) for 144 hours, with differences observed in the inhibitor immersion times of 24, 72, and 168 hours. In particular, an analytical error prevents the 120-hour immersion period in corrosive media from being displayed. As shown in Figure 3, the XRD characterisation data are represented as a diffractogram between the intensity and the angle of 2θ . The measured diffraction angle is plotted on the x-axis, and the peak intensity is plotted on the y-axis in this XRD characterisation

data peak-to-peak graph. Using the search match analysis method or data matching method, the intensity data and diffraction peak positions obtained from the XRD analysis were compared with reference data from the ICDD (International Centre for Diffraction Data) to determine the crystalline phases and compounds present in the immersing steel samples.

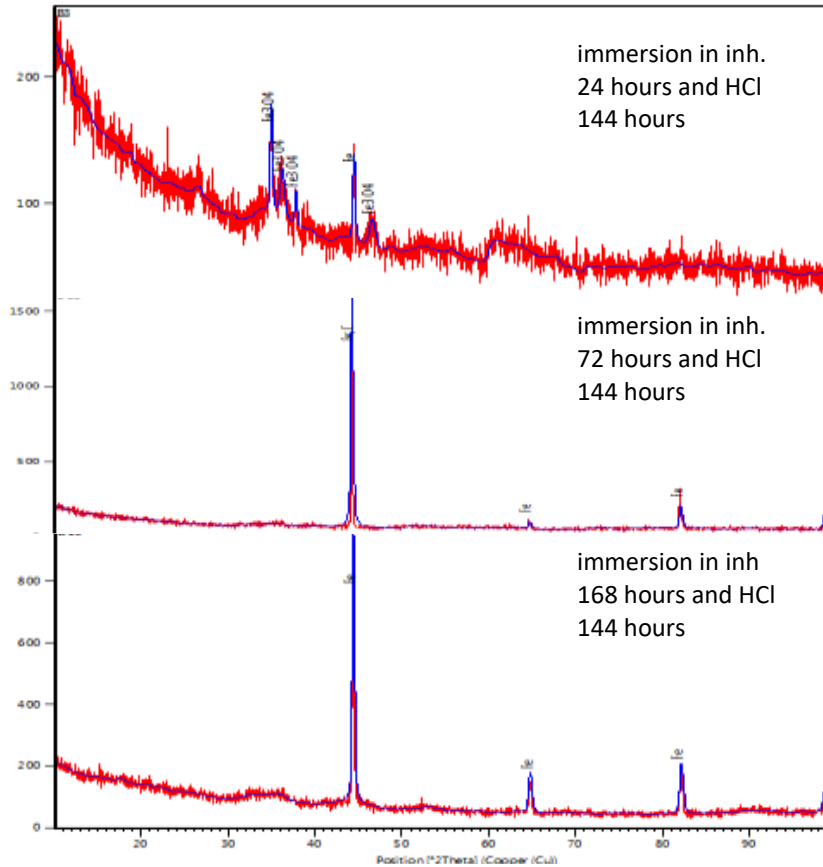


Figure 3. XRD characterisation results for samples at variation time (hour) of inhibitor in the corrosive medium HCl 1.5M for 144 hours (a) 24, (b) 72, and (c) 168.

Table 2: 2θ value and highest peak intensity XRD curves of steel samples immersion in inhibitors for 24 hours in 1.5M HCl for 144 hours

Peak	2θ	Intensity	Phase
1	35.0251	100.00	Fe ₃ O ₄
2	36.2815	44.67	Fe
3	37.8466	32.74	Fe ₃ O ₄
4	44.5142	83.68	Fe ₃ O ₄
5	46.6377	25.79	Fe ₃ O ₄

The sample with the highest corrosion rate had magnetite (Fe₃O₄) as an excessive corrosion product, according to the first section of the XRD characterisation data. The interaction between Fe and OH forms the magnetite phase [14]. The peak of Fe₃O₄ at position 2θ, specifically at 35.0251° with an intensity of 100%, is where the intensity is maximum. At

point 2θ , which is 46.6377° and has an intensity of 25.79%, the fifth peak which is also the peak of Fe_3O_4 has the lowest intensity. Due to high corrosion and lack of inhibitor coating on the steel surface, the first graph in Figure 3 and Table 2 shows that the first, third, fourth, and last peaks in this sample are magnetite (Fe_3O_4) phases, while the second peak is iron (Fe) phases [13],[9].

Table 3: Main peak XRD curve of steel samples immersion in inhibitors for 72 hours in 1.5M HCl for 144 hours

Peak	2θ	Intensity	Phase
1	44.3699	100.00	Fe, C
2	64.7198	14.85	Fe
3	82.1028	20.30	Fe
4	98.6537	9.70	Fe

Table 4: Main peak XRD curves of steel samples immersion in inhibitors for 168 hours in 1.5M HCl for 144 hours

Peak	2θ	Intensity	Phase
1	44.2716	100.00	Fe
2	64.6859	3.35	Fe
3	82.0503	11.89	Fe
4	98.6194	8.82	Fe

The XRD testing findings for the two samples from the peaks of the XRD graphs are the same and do not significantly differ, as can be seen in Figure 3's second and third parts. Each one generates four extreme peaks, which signify the crystalline phase's creation. As seen by Table 3, the resulting intensity for the C and Fe phases is 100% at the 2θ location of 44.3699° , indicating that these phases are very high, whereas the Fe phase is produced for the other three peaks. According to [4], the sample has a high concentration of iron and carbon due to its prolonged immersion in the inhibitor for 168 hours, which resulted in an interaction between iron and tannin components from cocoa pod extract.

As shown in Figure 3, which has four distinct peaks with the highest intensity at position 2θ 44.2716° and the lowest intensity at position 2θ 98.6194° at 8.82%, the XRD characterisation results for the samples indicated in Table 4 are not significantly different. The samples with the most significant difference in the immersion period in the inhibitor and HCl have four peaks with the same phase, namely Fe. This suggests that the sample retains a high concentration of iron, consistent with the study by [16], which found low-carbon steel to be the source of the Fe phase.

3.3 Analysis of AFM

The outcomes of the AFM study show that the adsorption generated on the steel surface is formed progressively, as indicated by the longer immersion duration of the used inhibitor. As the steel surface is submerged in the

inhibitor for extended periods, adsorption forms on it (Figure 4). Tannins from the extract can combine with the thin adsorption layer on the surface. The complex that forms can resist attacks from ions that cause corrosion to the steel surface, allowing it to endure the rate of corrosion [10], [17], [18], and [19].

The effect of applying and adsorbing cocoa shell extract on the steel's surface is shown in Figure 4. The untreated steel surface is depicted in Figure 5a. On the other hand, figure 4b illustrates the severely damaged steel surface resulting from immersion in the corrosive medium HCl without first submerging in the inhibitor. The inhibitor's ability to slow down the corrosion rate was evident when the sample was submerged for four distinct intervals of 24, 72, 120, and 168 hours. This is because the steel undergoes adsorption on its surface following its immersion in the inhibitor. A thin layer created by the adsorption of cocoa pod extract on the steel surface can slow the pace at which the corrosive medium corrodes [5], [8], [14]. Figures 5c–5f show the outcomes of the surface-formed protection.

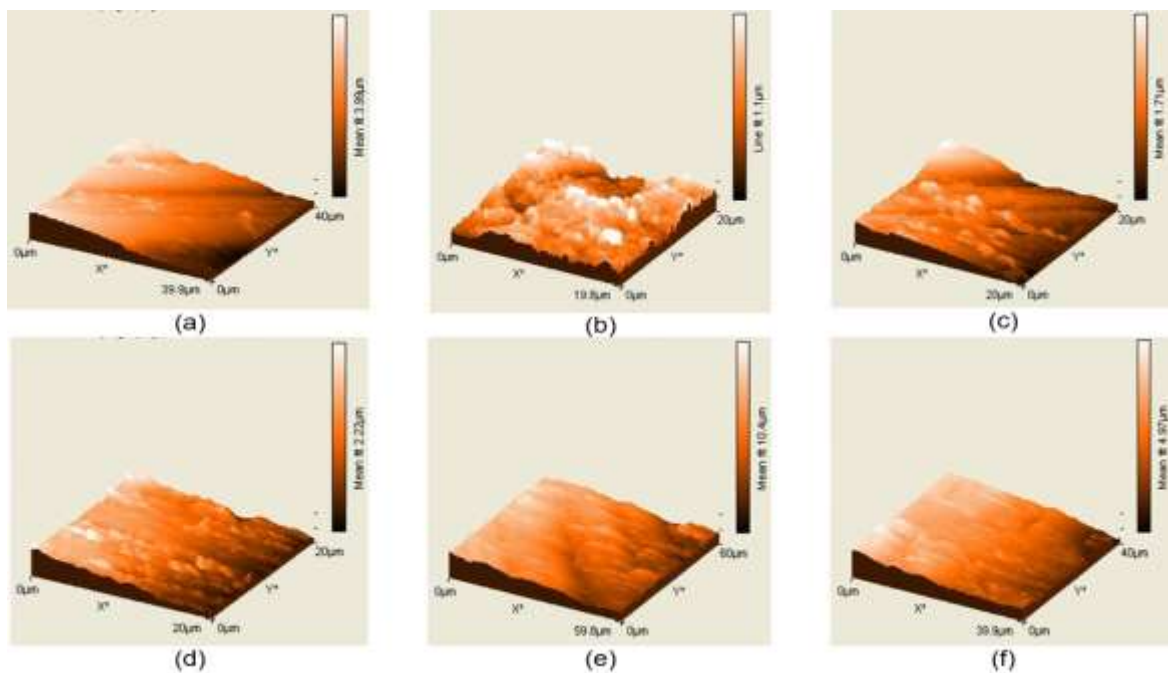


Figure 4: Morphological of steel surfaces using an AFM (a) without Treatment, (b-f) Treatment in variations in immersion time in inhibitors. (b) without inhibitors (c) 24 hours (d) 72 hours (e) 120 hours (f) 168 hours with 1.5M HCl medium

3.4 Tannin and Tannin-Fe Compound Structure

One substance that can stop corrosion on a metal surface is a corrosion inhibitor, and tannin is one such substance. Because tannin compounds have π electrons and lone pairs of electrons in their chemical structure, they can be utilised as inhibitors. Using the B3LYP/6-31G basis set and the DFT approach, Gaussian 16W was applied to optimise the tannin compound.

The molecular structure, ideal geometric structure, and HOMO and LUMO contours for tannin-Fe and pure tannin compounds are displayed in Figures 5 and 6. Absorption centres and interactions amongst inhibitor molecules can be predicted using the HOMO and LUMO outlines. The HOMO contour shows the LUMO contour shows areas that are electron donors and areas that are electron acceptors. The HOMO and LUMO outlines are centred on tannin molecules, as seen in Figure 5. While Figure 6 demonstrates that the HOMO and LUMO contours are centered on tannin compounds containing Fe atoms, this suggests that tannin compounds have favorable qualities as electron donors and acceptors. This explains why there will be an excellent donor and electron transfer between tannin molecules and Fe when tannins react with Fe [15], [7].

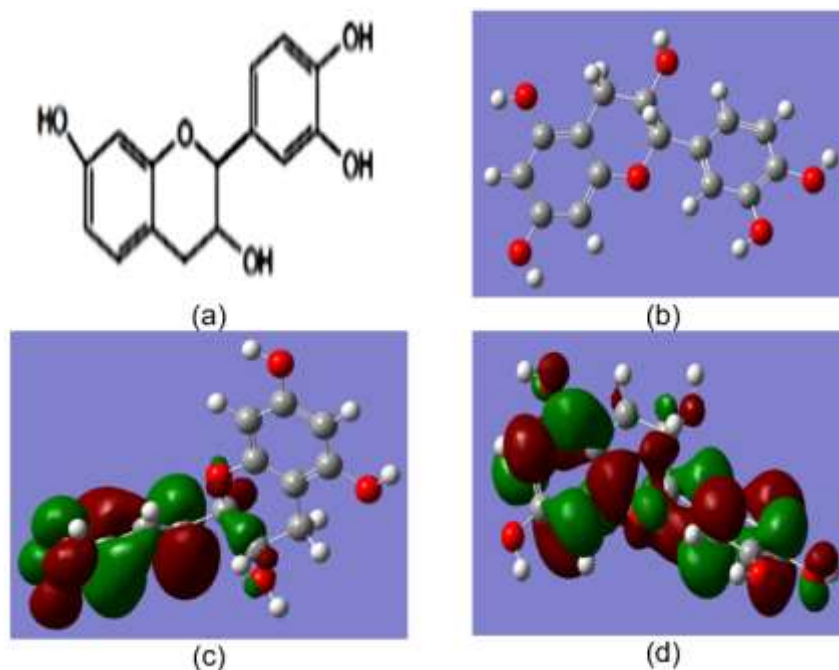


Figure 5: Process of tannin compound optimisation, (a) Structure of molecular (b) Structure of geometry, (c) Contour of HOMO, and (d) Contour LUMO

The ability of a molecule to donate electrons is represented by its HOMO energy. A molecule's HOMO energy increases with its ability to donate electrons, whereas its LUMO energy indicates its ability to accept electrons. The LUMO energy decreases as the molecule's electron-taking efficiency increases. According to [20], [21], [22], the inhibitor molecule works by donating one pair of electrons to ferrous metal, making the more reactive inhibitor the one with the larger LUMO energy and larger HOMO energy.

The DFT-B3LYP/6-31G method was used to calculate the tannins' corrosion inhibition efficiency (EI%). With this method, the theoretical EI (EI_{theory}) is 80.21%, I_{Add} is 7.36%, and EI_{Add} is 0.055%. Where I_{add} is the percentage of the ionisation potential of tannin compounds, EI_{add} is the percentage of corrosion inhibition efficiency of tannin inhibitor compounds, and EI_{theory} is theoretical

corrosion inhibitor efficiency. These results demonstrate that the maximum inhibition effectiveness findings obtained in a study utilising the weight loss method are 74.71%. However, quantum chemical calculations give a high inhibition efficiency for tannin compounds, namely 80.21%. This indicates that tannin compounds can inhibit or reduce the rate of steel corrosion by forming complex compounds with iron, thereby covering and protecting the steel surface. The results of experiments and tests using the Gaussian software are not significantly different due to corrosion attacks [23], [24].

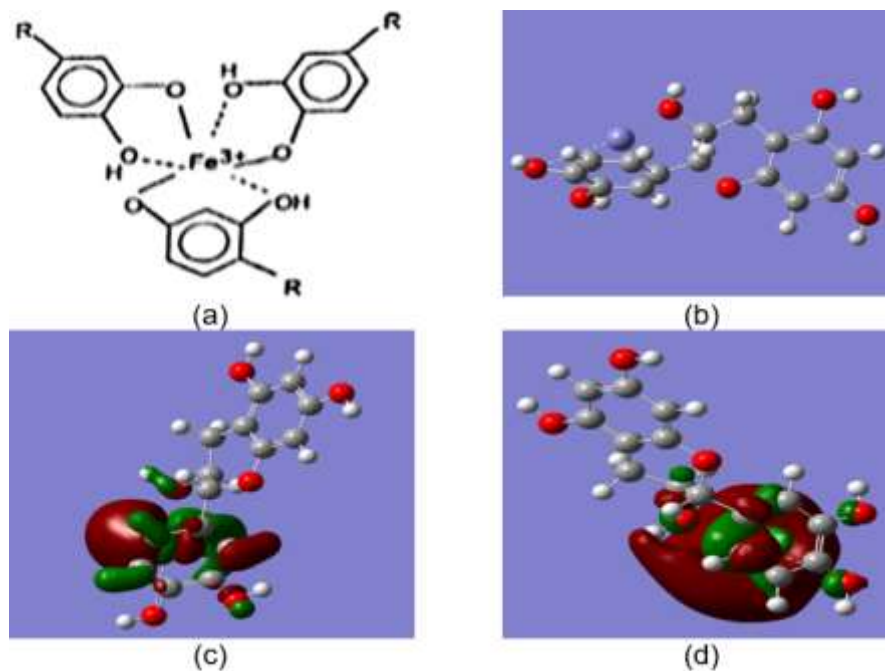


Figure 6: Optimization process for tannin-Fe compounds, (a) Molecular structure (b) Geometry structure (c) HOMO Contour, and (d) LUMO Contour

4.0 Conclusion

Based on the research findings, the following conclusions can be drawn. Firstly, cocoa pod extract has shown strong potential as a corrosion inhibitor for steel. Secondly, the immersion time in the inhibitor is inversely related to the corrosion rate in a corrosive medium under consistent conditions of time and concentration. The corrosion rate decreases as the immersion duration increases, with samples immersed for 168 hours demonstrating the lowest corrosion rate and an inhibition efficiency of 74.71%. Thirdly, the morphology of samples exposed to 1.5 M HCl for 144 hours, analysed using optical and scanning electron microscopy (SEM), revealed that longer immersion times enhance adsorption on the steel surface. XRD analysis identified that samples with the highest corrosion rates exhibited a crystalline magnetite phase, whereas prolonged immersion resulted in the formation of Fe and C phases, indicating reduced corrosion. Lastly, quantum chemical characterisation confirmed the interaction between tannin compounds in the extract and Fe, achieving an inhibition efficiency of 80.21%, as evidenced by molecular structure, geometry, and electronic properties such as EHOMO and ELUMO. These findings suggest significant potential for the commercialisation of cocoa

pod extract as an eco-friendly corrosion inhibitor for industrial use. Future research should focus on scaling up production, optimizing formulations and concentrations for various corrosive environments, and evaluating long-term performance and economic feasibility to advance its industrial application.

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Author Contributions

Yuli Yetri: Conceptualization, Methodology, Software, Validation, Formal Analysis, Investigation, Data Curation, Writing – Original Draft Preparation, Writing – Review and Editing; **Dahyunir Dahlan:** Data Curation, Validation, Supervision, Funding Acquisition, Resources, Project Administration; **Rakiman, Maimuzar:** Resources, Project Administration; **Wan Mohd Norsani Wan Nik:** Resources.

Conflicts of Interest

The manuscript has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission, and declare no conflict of interest in the manuscript.

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