

## Reduction of Steel Corrosion Rate Using Natural Inhibitor from Cocoa Pod Husk Extract in HCl Solution

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### Abstract

This study explores the effectiveness of cocoa husk extract as a natural corrosion inhibitor for steel exposed to hydrochloric acid (HCl). The experiment was conducted in two main stages: first, the steel specimens were immersed in cocoa husk extract solution for four different durations (48, 96, 144, and 192 hours) to allow the formation of a protective layer on the metal surface. Second, the treated specimens were immersed in 1 M HCl solution for 168 hours to assess their corrosion resistance. The corrosion rate was assessed using the weight loss method, which quantifies mass reduction as an indicator of corrosion severity. Surface characteristics were analyzed through optical microscopy, Scanning Electron Microscopy (SEM), and theoretical modeling using Density Functional Theory (DFT). The findings demonstrate that the application of cocoa husk extract significantly reduces corrosion rates, with a maximum inhibition efficiency of 78.4%. This improvement is attributed to the formation of a protective layer on the steel surface, which acts as a barrier against acid interaction. The results suggest that cocoa husk extract is a promising, environmentally friendly alternative for protecting steel materials from corrosion.

**Keywords:** Corrosion Rate, Cocoa, HCl, Weight Loss, SEM, DFT.

### INTRODUCTION

Corrosion is a major challenge in the utilization of steel across various industrial sectors, particularly when steel is exposed to acidic environments such as hydrochloric acid (HCl) solutions. The corrosion process not only leads to a reduction in the structural integrity of the material but also results in significant economic losses due to maintenance costs and the replacement of damaged components. (Iziorworu et al.2020).

One approach to reducing the corrosion rate was demonstrated by Popoola et al. (2021), who employed corrosion inhibitors that form a protective layer on the metal surface. However, many synthetic inhibitors currently in use have adverse effects on the environment and human health. Therefore, the search for environmentally friendly alternative inhibitors has become a focus of recent research.

Cocoa pod husk extract (*Theobroma cacao*) has shown potential as a natural corrosion inhibitor. A study by Yetri et al. (2013) demonstrated that the polar extract of cocoa pod husk can reduce the corrosion rate of mild steel in HCl solution, achieving an inhibition efficiency of up to 96%. In addition, a study by Rahman et al. (2023) found that cocoa pod husk extract is effective in inhibiting steel corrosion in various corrosive media, including rainwater and seawater, with a maximum inhibition efficiency of 93.06%.

The inhibition mechanism of cocoa pod husk extract is presumed to involve the adsorption of active compounds such as tannins and polyphenols onto the steel surface, forming a protective layer that impedes the interaction between the metal and the corrosive environment. This is supported by a study conducted by Yetri et al. (2024), which demonstrated that immersing steel in cocoa pod husk extract for a specific duration can enhance corrosion resistance, as analyzed using the

weight loss method, optical microscopy, scanning electron microscopy (SEM), and Density Functional Theory (DFT) simulations.

Based on this background, the present study aims to evaluate the effect of steel immersion duration in cocoa pod husk extract on the corrosion rate when exposed to HCl solution. By understanding the relationship between immersion time and inhibition efficiency, this research is expected to contribute to the development of an effective and environmentally friendly method for steel protection.

## MATERIALS AND METHODS

This study utilized low-carbon steel specimens measuring  $2 \times 2 \times 0.2$  cm as the primary material for corrosion testing. The natural corrosion inhibitor used was cocoa (*Theobroma cacao*) pod husk extract, obtained from dried agricultural waste collected in the Pariaman region, West Sumatra. The extraction of active compounds from the cocoa husk was carried out using 70% ethanol as the solvent. The corrosive medium was prepared by diluting concentrated hydrochloric acid (HCl, 37% purity, Dwiraga, Padang) to obtain a 1 M HCl solution. The instruments and equipment used in this research included a high-precision digital balance ( $\pm 0.1$  mg), optical microscope, Scanning Electron Microscope (SEM), and simulation software based on Density Functional Theory (DFT). A rotary evaporator was employed for extract concentration. Additional laboratory tools included sandpapers of varying grit sizes (400–1200), measuring cylinders, Erlenmeyer flasks, beakers, and a magnetic stirrer.

The cocoa pod husks were first dried, finely ground, and then subjected to maceration extraction using 70% ethanol for 72 hours. The resulting mixture was filtered, and the filtrate was concentrated using a rotary evaporator to obtain a thick extract. Low-carbon

steel samples were prepared by polishing the surface with progressively finer grades of sandpaper (400–1200 grit), followed by washing with ethanol and distilled water. The samples were then dried and weighed to determine the initial mass ( $m_0$ ). To facilitate the formation of a protective layer, the steel samples were immersed in the cocoa husk extract for four different durations: 48, 96, 144, and 192 hours. After immersion, the samples were dried and prepared for subsequent corrosion testing.

Corrosion testing was carried out by immersing the coated steel samples in 1 M hydrochloric acid (HCl) solution for a fixed duration of 168 hours. After immersion, the samples were cleaned to remove corrosion residues, dried thoroughly, and then reweighed to obtain the final mass ( $m_2$ ). The corrosion rate was determined using the weight loss method, calculated according to the following equation:

$$\text{Corrosion Rate} = \Delta m / A t,$$

where  $A$  is the surface area of the sample and  $t$  is the immersion time. The inhibition efficiency was calculated by comparing the corrosion rate of uncoated steel with that of the treated samples. To support the analysis, surface characterization was performed using optical microscopy and Scanning Electron Microscopy (SEM), as reported in the study by Zainal et al. (2022). Furthermore, the interaction between the active compounds and the metal surface was investigated through simulations based on the Density Functional Theory (DFT) approach.

## RESULTS AND DISCUSSION

Based on the results of the study, Figure 1a illustrates the relationship between the immersion time of steel in cocoa pod husk extract as a corrosion

inhibitor and the corrosion rate of the steel in HCl solution. The data indicate that the longer the immersion duration, the lower the corrosion rate observed. At 48 hours of immersion, the corrosion rate reached 1.0412 mg/cm<sup>2</sup>·h, which was the highest value recorded in this study. After 96 hours, the corrosion rate decreased to 0.6771 mg/cm<sup>2</sup>·h, indicating the initial effectiveness of the protective film formed by the active compounds in the cocoa husk extract. This downward trend continued with a corrosion rate of 0.5469 mg/cm<sup>2</sup>·h at 144 hours, reaching the lowest value of 0.3906 mg/cm<sup>2</sup>·h after 192 hours of immersion. This gradual reduction suggests that the adsorption process of inhibitory compounds such as tannins, flavonoids, and polyphenols became increasingly stable and dense with longer contact time on the steel surface. The progressively formed passive layer inhibits the diffusion of aggressive ions such as H<sup>+</sup> and Cl<sup>-</sup> toward the metal surface, thereby slowing down the electrochemical reactions responsible for corrosion (Zainal et al., 2022). These results reinforce the evidence that cocoa pod husk extract can serve as an effective natural corrosion inhibitor and offer a sustainable approach to metal protection in acidic environments.

Figure 1b presents the observed relationship between immersion time and inhibition efficiency. The data reveal a non-linear, exponentially shaped decreasing trend in corrosion rate, while inhibition efficiency shows a progressive increase approaching saturation. This behavior suggests time-dependent adsorption kinetics, where longer immersion durations directly correspond to increased inhibition efficiency. At 48 hours of immersion, the inhibition efficiency reached 37.5%, indicating the initial formation of a protective layer on the metal surface. This early-stage film formation marks the beginning of the interaction between

the active compounds in the cocoa pod husk extract and the steel substrate, leading to the suppression of corrosion processes. As the immersion time increased to 96 hours, the inhibition efficiency rose to 53.8%, indicating that the active compounds in the cocoa pod husk extract began to adsorb more uniformly onto the steel surface. A further increase was observed at 144 hours, with the efficiency reaching 66.1%, and ultimately achieving a maximum value of 78.4% at 192 hours.

This trend suggests that prolonged exposure of the metal to the inhibitor solution enhances the likelihood of interaction between the organic compounds in the extract and the metal surface (Rahman et al., 2023). Compounds such as tannins, flavonoids, and other phenolic constituents are believed to play an active role in the formation of a passive film that suppresses the corrosion process through an adsorption mechanism. The time-dependent increase in inhibition efficiency supports the hypothesis that the protection mechanism is kinetically controlled and relies on sufficient contact time between the inhibitor molecules and the metal substrate. Therefore, immersion duration emerges as a critical parameter in the effective and sustainable application of natural product-based corrosion inhibitors.

Based on the two presented graphs, a complementary relationship is evident between the immersion duration of the metal in the cocoa pod husk extract-based inhibitor solution and both the reduction in corrosion rate and the increase in inhibition efficiency. The first graph demonstrates a significant decrease in corrosion rate with increasing immersion time. At 48 hours, the corrosion rate remained relatively high at 1.0412 mg/cm<sup>2</sup>·h. However, this rate gradually declined to 0.3906 mg/cm<sup>2</sup>·h after 192 hours of immersion. This trend aligns with the second graph,

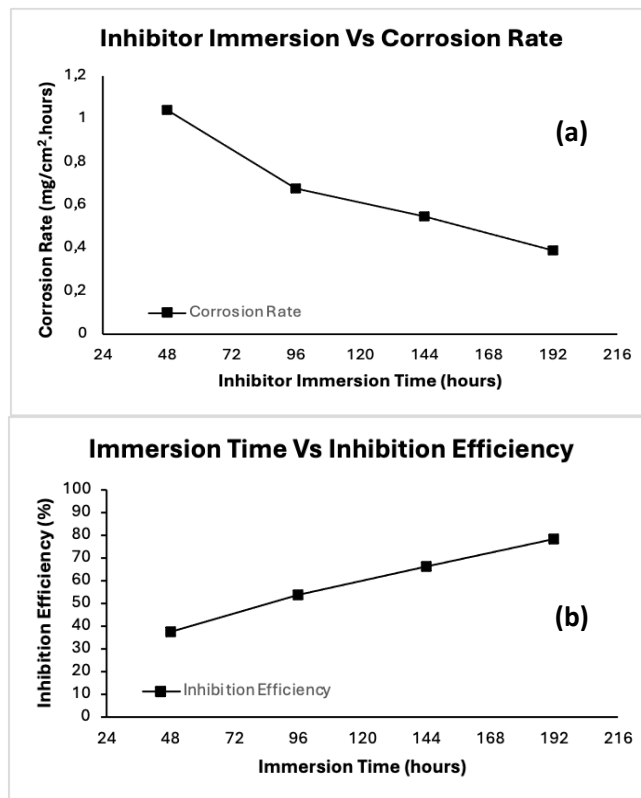


Figure 1. (a) Graph of Inhibitor Immersion Time versus Corrosion Rate  
(b) Graph of Inhibitor Immersion Time versus Inhibition Efficiency

which shows an increase in inhibition efficiency from 37.5% at 48 hours to 78.4% at 192 hours. This relationship indicates that the longer the metal is immersed in the inhibitor solution, the greater the ability of the active compounds in the extract to form a protective layer on the metal surface (Zainal et al., 2022). This layer acts as a barrier to the diffusion of corrosive ions, such as chloride and protons, which are key contributors to metal degradation (Zainal et al., 2022). The concurrent increase in inhibition efficiency and decrease in corrosion rate suggests that the adsorption of organic inhibitor compounds is both time-dependent and accumulative in nature (Yetri et al., 2015). Thus, the two graphs collectively reinforce the conclusion that immersion duration is a critical factor in determining the

effectiveness of natural inhibitors for corrosion protection.

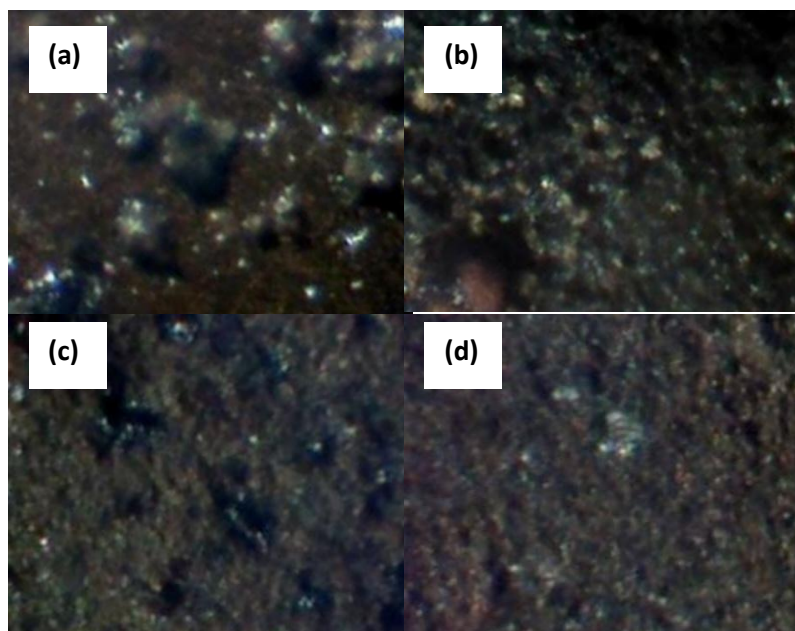
Analisis morfologi permukaan baja Observations using an optical microscope are presented in Figure 2. Figure 2a shows the surface of the steel sample, which still exhibits signs of corrosion despite having been treated with a coating of cocoa pod husk extract. The metal surface displays several damage points resembling pitting corrosion—small holes formed as a result of localized attack by aggressive ions such as  $\text{Cl}^-$  in the HCl solution. The presence of this damage suggests that although the inhibitor is active, the coating has not yet fully and uniformly covered the entire metal surface. However, the limited spread and depth of the corrosion defects indicate a reasonably significant protective effect provided by the active compounds in the extract.

The second steel sample exhibits a more degraded surface condition. As shown in Figure 2b, the surface texture appears rougher and more heterogeneous, accompanied by discoloration in several areas, which are likely the result of corrosion product formation, such as iron oxides or hydroxides. This condition suggests that at certain points, the protective effectiveness of the inhibitor layer has diminished, possibly due to prolonged immersion duration or uneven distribution of the coating.

In contrast, the steel sample in Figure 2c shows a more stable metal surface condition. Corrosion appears to be less severe, with a more uniform surface texture and minimal evidence of deep damage. This indicates a higher level of inhibition effectiveness, likely due to the successful interaction of active compounds—particularly tannins—from the cocoa pod husk extract. These compounds are believed to form more stable chemical bonds

with the steel surface, resulting in the formation of a passive layer that inhibits direct contact between the metal and the acidic solution (Popoola, 2021).

The steel surface in Figure 2d appears to be in the best condition. Almost no visible corrosion pits are observed, and the surface displays a more homogeneous color and texture. This suggests that the inhibitor layer functioned optimally in this region, effectively protecting the steel from corrosive attack. The tannins present in the cocoa pod husk play a key role in forming this protective layer. As polyphenolic compounds containing hydroxyl ( $-OH$ ) and carbonyl groups, tannins are capable of bonding with metal ions on the steel surface through complexation or adsorption interactions (Iziorworu et al., 2020). These interactions lead to the formation of a thin protective film that acts as both a physical and chemical barrier against the penetration of  $H^+$  and  $Cl^-$  ions from the HCl solution.



**Figure 2. Optical microscope images of steel surfaces**

- (a) steel immersed for 48 hours,
- (b) steel immersed for 96 hours,
- (c) steel immersed for 144 hours,
- (d) steel immersed for 192 hours.

Overall, surface morphology observations across the four images demonstrate that cocoa pod husk extract containing tannins can effectively function as a natural corrosion inhibitor. Tannins not only form stable bonds with the metal surface but also possess antioxidant properties that help prevent further oxidative reactions. Therefore, their application as a protective coating offers an environmentally friendly and efficient solution for reducing the corrosion rate of steel in acidic environments.

Surface morphology analysis of the steel using Scanning Electron Microscopy (SEM) revealed that coating with cocoa pod husk extract significantly reduced the severity of corrosion in HCl solution. At 48 hours

of treatment (Figure 3a), the steel surface still exhibited active damage in the form of pitting and fine cracks, indicating that the protective layer had not yet formed uniformly. However, with increased coating duration—particularly at 96 hours (Figure 3b) and 144 hours (Figure 3c)—the metal surface appeared smoother and more homogeneous, suggesting the development of a more stable and effective inhibitor layer. This condition reached its optimum at 144 hours, where the surface morphology showed minimal visible damage, indicating successful adsorption of active compounds in the cocoa extract, especially tannins, which contributed to the formation of a passive film on the metal surface.

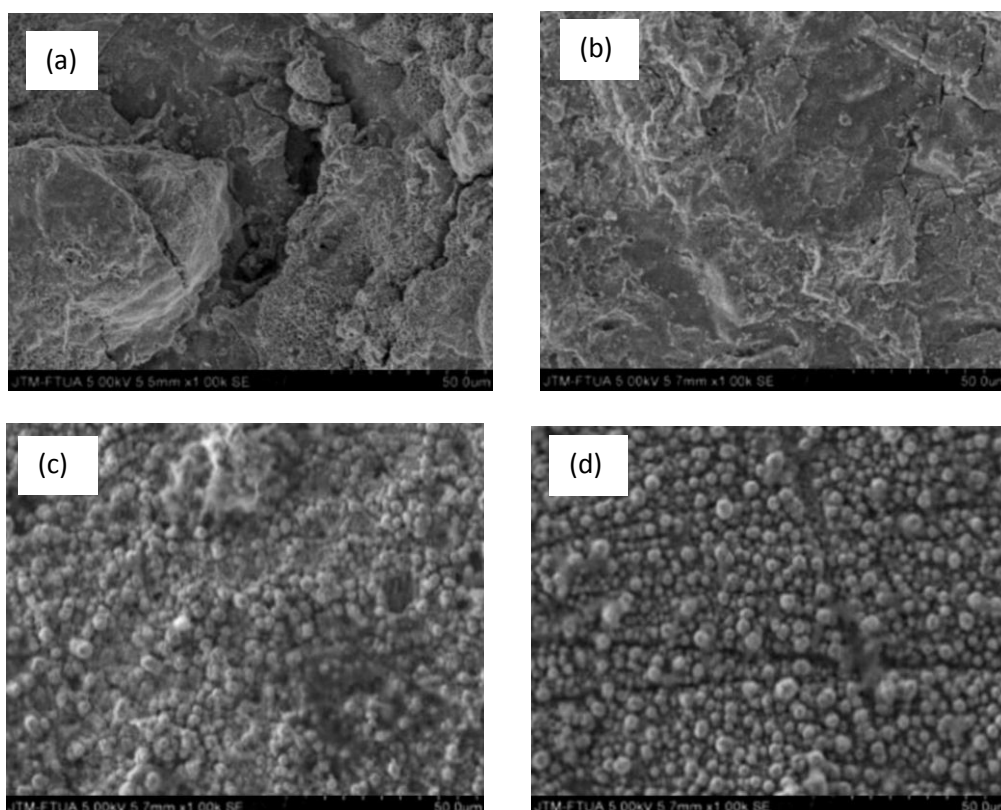


Figure 3. SEM image of :  
(a)Steel immersed for 48 hours,  
(b)Steel immersed for 96 hours,  
(c)Steel immersed for 144 hours,  
(d)Steel immersed for 192 hours.

After 192 hours of coating (Figure 3d), the steel surface remained well protected, although slight irregularities in texture began to appear—possibly due to minor degradation of the protective layer resulting from prolonged exposure to the corrosive solution. The successful formation of this protective film is attributed to the presence of tannins in the cocoa pod husk extract, which contain hydroxyl and carbonyl functional groups capable of binding to metal ions. These interactions lead to the formation of an adsorbed film that inhibits direct contact between the steel surface and aggressive ions such as  $H^+$  and  $Cl^-$ .

Overall, these results demonstrate that cocoa pod husk extract is an effective and environmentally friendly corrosion inhibitor, capable of providing long-term protection for metals in acidic environments.

The structural and electronic properties of the tannin molecule were

analyzed using the Density Functional Theory (DFT) method to evaluate its potential interaction with metal surfaces in the context of corrosion inhibition. The optimized molecular geometry of tannin is presented in a ball-and-stick model. Carbon, oxygen, and hydrogen atoms are represented in gray, red, and white, respectively, while the presence of a purple atom may indicate the involvement of a metal ion or another polar substituent. The molecular structure shown in Figure 4a reveals a high density of aromatic hydroxyl and carbonyl groups evenly distributed across the ring framework. These functional groups act as electron-donating centers that facilitate interactions with the metal surface. The abundance of these groups enhances tannin's ability to form coordination bonds with active metal sites, thereby supporting its role as an effective corrosion inhibitor (Zainal et al., 2022).

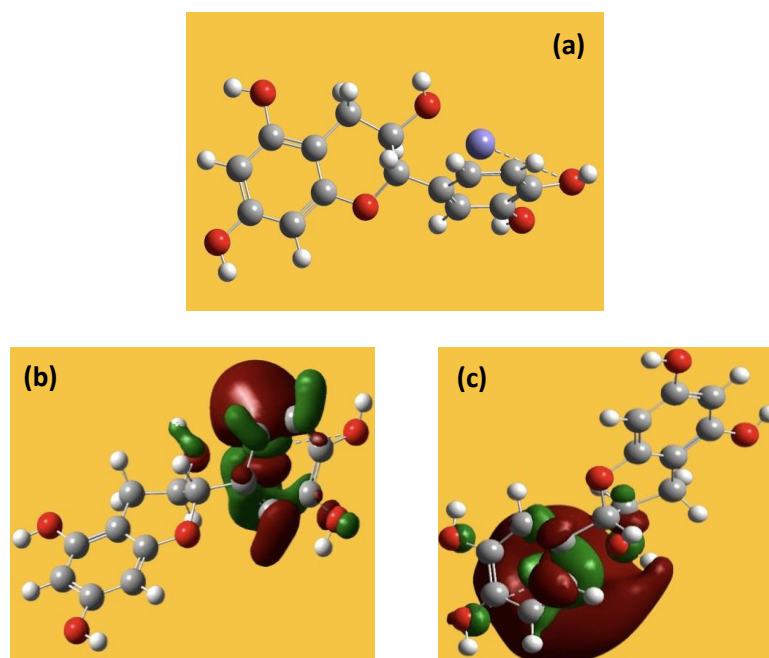


Figure 4. DFT analysis of the tannin molecule:  
(a) Optimized molecular geometry of tannin,  
(b) Highest Occupied Molecular Orbital (HOMO),  
(c) Lowest Unoccupied Molecular Orbital (LUMO).

Furthermore, the molecular orbital visualizations are presented in Figure 4b and Figure 4c, corresponding to the electron density distribution of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), respectively. The HOMO orbital, illustrated in green and red regions, indicates that the highest-energy electrons are primarily localized around the phenolic and carbonyl functional groups. This suggests that these regions serve as potential sites for electron donation to the metal surface, supporting the adsorption mechanism. Meanwhile, the LUMO distribution, as shown in Figure 4c, also reveals localization in similar regions, indicating the molecule's capacity to accept electrons at these sites. This overlap implies the potential for donor-acceptor interactions during chemisorption. The relatively narrow energy gap between the HOMO and LUMO orbitals, along with their localized distribution, reflects the electronic stability of the molecule and supports the efficiency of tannins as corrosion inhibitors via electronic interactions with the metal surface, particularly in acidic environments such as HCl.

This theoretical analysis reinforces the experimental evidence that tannins present in cocoa pod husk extract actively contribute to the formation of a protective layer on the steel surface. The molecular structure of tannins, which is rich in hydroxyl and carbonyl groups, facilitates the formation of coordination bonds between the inhibitor molecules and metal ions on the steel surface. The HOMO visualization confirms that these functional groups serve as primary electron-donating centers, enabling the development of a stable protective film. Conversely, the LUMO distribution—

also concentrated in the same regions—indicates the molecule's ability to accept back-donated electrons from the metal, leading to strong bidirectional (donor-acceptor) interactions. This interaction supports the formation of an adsorbed layer capable of effectively impeding the diffusion of corrosive ions such as  $H^+$  and  $Cl^-$ . The low estimated energy gap between HOMO and LUMO further suggests that the tannin molecule possesses high chemical reactivity and a strong tendency for chemisorption. This correlation aligns with the experimental results, which demonstrated increased inhibition efficiency and significantly reduced corrosion rates after prolonged immersion. Thus, the DFT simulation not only highlights the structural potential of tannins but also provides a solid theoretical foundation for understanding the corrosion inhibition mechanism of cocoa pod husk extract at the molecular level.

## CONCLUSION

This study demonstrates that cocoa pod husk extract functions effectively as a natural corrosion inhibitor for mild steel in hydrochloric acid solution, achieving a maximum inhibition efficiency of 78.4% after 192 hours of immersion. The corrosion rate decreased significantly from 1.0412  $mg/cm^2 \cdot h$  to 0.3906  $mg/cm^2 \cdot h$ , indicating a substantial protective effect attributed to the formation of a passive layer on the steel surface.

This effectiveness is attributed to the formation of a protective layer composed of active compounds such as tannins, flavonoids, and polyphenols present in the cocoa pod husk extract. This layer acts by inhibiting direct interaction between corrosive ions and the steel surface. Visual analysis using optical microscopy and SEM, along with theoretical insights from Density

Functional Theory (DFT), supports the crucial role of these compounds in establishing a stable and comprehensive protective barrier on the metal.

Cocoa pod husk extract demonstrates significant potential for

development as a green corrosion inhibitor, replacing conventional synthetic chemical compounds that have long been used and are often associated with adverse effects on both human health and the environment.

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