Mangrove bark tannins as a Zn–P coating sealant for mild steel corrosion protection in 3.5% NaCl solution

Shahadad Zainol Abidin © and M Hazwan Hussin ©
Materials Technology Research Group (MaTReC), School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
E-mail: mhh@usm.my and mhh.usm@gmail.com
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Abstract
In this work, mangrove bark tannins have been studied as a sealant after Zn–P of mild steel. The efficiency of the sealant against the corrosion was tested by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PD) in 3.5% NaCl solution. The increased in the concentration of the tannin as a sealant increases the inhibition efficiency up to optimum concentration of 4 g l⁻¹. The inhibition efficiencies of tannin methanol extract (TME) and 70% tannin acetone extract (TAE) were 83.52% and 71.12% respectively. The results obtained from EIS and PD were in a good agreement and complementary to each other. The double layer constant phase element (CPE dl) decrease indicated that a film form on the surface of the mild steel that retard the corrosion activities. Further, the pore modifications and elemental compositions were analyzed by scanning electron microscope (SEM) and energy dispersive x-ray (EDX).

1. Introduction

Mild steel is one of the important raw materials in industry as it serves for various applications. It is widely used due to its affordable cost. However, one of the most serious problems in the industry is the corrosion of mild steel itself [1]. The global cost of corrosion estimated at approximately USD 2.5 trillion that equal to 3.4% GDP (Gross Domestic Product). Global savings between 15%–35% due to corrosion cost of damage can be achieved by implementing practices of corrosion prevention [2]. In Malaysia, the cost of corrosion is around RM 6.7 billion from RM 2017.4 billion of GDP annually [3].

Phosphating is widely used metal pretreatment process [4]. It is simple and famous preliminary coating of carbon steel, zinc, aluminium, cadmium and magnesium [5]. There are few types of phosphate coating such as zinc, manganese and iron phosphating coating. Phosphate coating form a layer of insoluble crystalline phosphate on the metal surface to be protected [6]. The layer formed increases the corrosion resistance [7]. However, adhesion of zinc phosphate coating on the surface of metal leads to formation of pore and micro-cracks [8] that decrease the corrosion resistance. Therefore, sealing the pores is an alternative to increase corrosion resistance [7].

Recently, tannins become famous due to its ability that can improve corrosion resistance of metal under highly conductive environments [9]. Tannins is an organic compound that is non-toxic and biodegradable. It is polyphenols presents in plant extracts. Sugars, ellagic acid, gallic acid and flavonoids are the basic components of tannin [10]. It is divided into two types that are hydrolysable tannin and condensed tannin. Derivatives of gallic acid (3,4,5- trihydroxy benzoic acid) is hydrolysable tannin where oligomeric and polymeric proanthocyanidins consist of coupled catechin units is condensed tannins [9]. Hydrolysable tannin is extracted from wood, pod and fruits of trees where condensed tannin is extracted from wood and bark of trees [11].

Condensed tannins consist of mainly flavonoids polymers and known as proanthocyanidins (PAs) [10]. In Malaysia, mangrove bark is one of the major sources of tannin. The tannin that extracted from mangrove bark (Rhizophora apiculata) species consist of four types of flavonoid monomers viz, epicatechin, epicatechin gallate, epigallocatechin, and catechin. The present of these types of monomers made the tannin of Rhizophora apiculata species as a condensed type tannin [12]. The purpose of this study was to investigate the use of tannin extracted...
from mangrove bark as a sealant after Zn-P of mild steel. Literature review shows that tannin extract from mangrove bark as a sealant has not been published yet.

2. Experimental

2.1. Materials

The mangrove (Rhizophora apiculata) barks were collected from charcoal industry in Kuala Sepetang, Taiping, Perak in September 2018. The mangrove barks were put under sun dried and ground to powder form. It then sieved through a 250 μm sieve and kept in a covered container.

Mild steel coupons (3 cm × 7 cm × 1 mm) were polished using silicon carbide paper up to grade #1000 and then degreased using acetone. (Mild steel elemental composition; C = 0.01%; Si = 0.16%; Mn = 0.15%; P = 0.01%; Al = 0.06%; Na = 0.02%; Mg = 0.03%; Fe = 99.56%). All the solvents and chemicals used were analytical AR grade with high purity.

2.2. Isolation of tannin from mangrove bark

The mangrove bark tannin were extracted using a method outlined by Rahim et al [13] with slight modifications. A mass of 10 g of finely ground mangrove barks mixed with 70% (v/v) aqueous acetone and shake at 110 rpm for 72 h (24 × 3 days). The mixture then filtered, and the filtrate was concentrated using rotary evaporator and followed by freeze-dried to get the tannin acetone extract (TAE). The same procedures were repeated using pure methanol as a solvent to extract the tannin (TME). The concentrated filtrate dried at 50°C for 24 h.

2.3. Zn-P coating

The prepared mild steel immersed in zinc phosphating bath at 80°C for 10 min and then rinsed with deionized water and dried [7]. The zinc phosphating bath was prepared based on a composition of 17.5 g l⁻¹, 20.0 g l⁻¹, 11.5 g l⁻¹, and 0.25 g l⁻¹ of phosphoric acid, nitric acid, zinc oxide, and nickel sulphate, respectively.

2.4. Sealing process

The Zn-P mild steel then immersed in different concentration of TAE (2, 4, 6, 8, 10 g l⁻¹) dissolved in distilled water for 40 min. The pH value of all the concentration was controlled close to pH 6.0 (optimal for formation of ferric-tannate) [7]. The method then repeated using TME as a sealant.

2.5. Studies of corrosion inhibition

2.5.1. Corrosion electrochemical test

Three-electrode cell system were used for the corrosion study. The cell assembled as mild steel coupon set as working electrode (WE) and the exposed area to the reaction was 3.142 cm². Platinum rod used as the counter electrode (CE) and saturated calomel electrode (SCE) used as reference electrode (RE). The electrolyte for the reaction used was 3.5% (wt.) NaCl solution. The treated and untreated mild steel performed electrochemical and polarization studies in a cell containing 50 ml of electrolyte. The distance of RE and WE are fixed throughout the studies. All the tests were repeated three times to ensure the reproducibility of the data.

2.5.2. Electrochemical impedance spectroscopy (EIS)

Corrosion resistance performance of Zn-P coating on mild steel that doped with different concentration of TAE and TME were analyzed by electrochemical impedance spectroscopy (EIS) using Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA (Gamry instruments, USA). The frequency range used are 10 kHz to 0.1 Hz. The EIS data obtained was analyzed using Gamry Echem Analyst version 6.33 software. The percentage of inhibition efficiency (%IE) calculated using equation (1) [14].

\[
\text{%IE} = \left( \frac{R_{ct(sample)} - R_{ct(blank)}}{R_{ct(sample)}} \right) \times 100
\]

where \( R_{ct(sample)} \) is charge transfer resistance (\( \Omega \) cm²) of the sample and \( R_{ct(blank)} \) is charge transfer resistance of the blank.

2.5.3. Potentiodynamic polarization

Corrosion parameters of Zn-P coating on mild steel that doped with different concentration of TAE and TME were analyzed by potentiodynamic polarization using Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA (Gamry instruments, USA). The potential scanning range was set between ±250 mV at scan rate of 0.5 mV s⁻¹. The percentage of inhibition efficiency (%IE) determined according to equation (2) [14].
where \( i_{\text{corr}}(\text{blank}) \) is corrosion current density (\( \mu \text{A cm}^{-2} \)) of the blank and \( i_{\text{corr}}(\text{sample}) \) is corrosion current density of the sample.

### 2.6. Surface analyses

#### 2.6.1. SEM/EDX

The surface morphologies of the tannin treated, and untreated zinc phosphate coated on mild steel analyzed using Scanning Electron Microscope (Quanta FEG 650, FEI). The analysis was carried out at different magnification and the beam voltage used was 15 kV. The morphologies of the samples were compared to each other. The elemental analysis was analyzed using EDX, Energy Dispersive x-ray analysis (X-Max 500 mm², Oxford).

#### 2.6.2. Water contact angle measurement

The hydrophobicity properties of the tannin treated, and untreated Zn-P coated on mild steel evaluated using KSV CAM 200 (KSV Instruments, Finland) wettability analyzer. A volume of 6.5 \( \mu \text{l} \) of distilled water dropped on the surface of each sample and the test carried out three times to ensure the reproducibility of the data. The dropped shape determined the contact angle of the samples that interpreted by Attension Theta software.

### 3. Results and discussion

#### 3.1. Isolation of tannin from mangrove bark

Tannin were extracted from mangrove bark using pure methanol and 70% aqueous acetone respectively. The extraction from 70% aqueous acetone produced brown powder of tannin (TAE) as shown in figure 1(A) with percentage yield of 27.17% ± 0.49. The extraction by using pure methanol produced black powder tannin (TME) shown in figure 1(B) and its percentage yield was 17.23% ± 0.86.

The percentage yield of tannin extraction using 70% aqueous acetone was higher compared to tannin extraction using pure methanol due to the difference in solvent polarity that affect the constituent’s solubility in each solvent [15]. The higher the polarity of the compound, the easier the compound to be extracted [16]. The present of water molecule in the 70% aqueous acetone, make it more effective in extracting the solute due to the higher polarity of water [17]. Where, the low polar solvent gives less percentage yield [15] such as pure methanol in this case. Thus, 70% aqueous acetone was the best solvent for the extraction of mangrove bark tannin compared to the pure methanol.

#### 3.2. Corrosion electrochemical test

Potentiodynamic polarization measurement provide information on classification of type of inhibitor either anodic, cathodic or mixed type. It also provides information on kinetics effects of anodic and cathodic reactions.

![Figure 1. Mangrove bark tannin powder.](image-url)
The evaluation of corrosion resistance behavior of coated and uncoated specimen also can be performed by potentiodynamic polarization technique [19]. EIS is a powerful technique for characterization of variety electrochemical systems in determination the effect of electrolytic process in the systems [20]. Open circuit potential measurements (OCP) were performed before performing polarization and impedance techniques. The purposes of OCP measurement is to define domains of corrosion, complete and partial inhibition, and determine threshold concentration of the inhibitors [18].

3.2.1. Electrochemical impedance spectroscopy (EIS)
In this study, the results were analyzed by Nyquist plots of impedance. Figure 2 shows the Nyquist plot for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE (figure 2(A)) and TME (figure 2(B)) in 3.5% (wt.) NaCl solution. The semicircle Nyquist plots indicated that the charge transfer existed at the electrode and the Nyquist plot diameter corresponded to the $R_{ct}$ [21]. The increase in the value of $R_{ct}$ increase the percentage of inhibition efficiency [22].
The experiment data of Nyquist plots fitted by two type of simple equivalent electrical circuit for bare mild steel in figure 3 and coated mild steel figure 4. In the circuit, Randle’s-CPE is used instead of Randle’s-Cdl to fit the semicircle accurately \[22\]. Impedance parameters presence in the equivalent circuit are \(R_s\), \(R_{ct}\), \(R_{coat}\), \(CPE_{dl}\) and \(CPE_{coat}\) which refer to solution resistance, charge transfer resistance, coating resistance, double layer constant phase element and coating constant phase element, respectively.

According to figure 2, the incorporation of tannin with Zn-P coated mild steel improved the corrosion inhibition efficiency. It can be seen that Zn-P coated mild steel with 4 g L\(^{-1}\) of both TAE and TME yielded the largest semicircle diameter of Nyquist plot indicated that at this concentration, the corrosion inhibition efficiency was at its best. Table 1 summarizes the electrochemical impedance parameters for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE in 3.5 wt% NaCl solution. The same parameters are summarized in table 2 for TME.

According to tables 1 and 2, the \(R_s\) value slightly vary with each other and this is due to the inconsistent distance between the reference electrode and working electrode while performing the analysis \[22\]. Moreover, as the concentration of tannin increased, the inhibition efficiency increased until it reached the optimum
Table 1. Electrochemical impedance parameters for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE in 3.5 wt% NaCl solution.

| Nature of mild steel            | $R_t$ (Ω cm$^2$) | $\text{CPE}_{\text{coat}}$ (μF cm$^2$) | $R_{\text{coat}}$ (Ω cm$^2$) | $\text{CPE}_{\text{dl}}$ (μF cm$^2$) | $R_{\text{dl}}$ (Ω cm$^2$) | % IE |
|--------------------------------|------------------|----------------------------------------|-----------------|------------------------------------|-----------------|-----|
| Bare mild steel                | 29.56            | —                                      | —               | 809.2                              | 1226.85         | —   |
| Zn-P                           | 27.28            | 535.5                                  | 83.11           | 538.5                              | 3701.28         | 67.04 |
| Zn-P + 2 g L$^{-1}$ TME        | 21.53            | 507.6                                  | 170.20          | 567.9                              | 4766.41         | 74.66 |
| Zn-P + 4 g L$^{-1}$ TME        | 23.16            | 265.7                                  | 207.52          | 235.0                              | 7261.16         | 83.23 |
| Zn-P + 6 g L$^{-1}$ TME        | 21.88            | 354.0                                  | 133.32          | 510.3                              | 5228.29         | 76.66 |
| Zn-P + 8 g L$^{-1}$ TME        | 19.54            | 517.7                                  | 27.67           | 565.0                              | 4936.08         | 74.79 |
| Zn-P + 10 g L$^{-1}$ TME       | 21.01            | 584.8                                  | 36.54           | 585.5                              | 4436.50         | 72.04 |

Concentration. This is due to the adsorption of inhibitor in the plant extract on the mild steel surface [23] and formed strength inhibitive film [24]. For both TAE and TME, the highest inhibition efficiency was at 4 g l$^{-1}$ tannin Zn-P coated mild steel that were 71.12% and 83.52% respectively and it was at the optimum. The further increase in the concentration after this optimum value the inhibition efficiency decreased due to the reduction of metal-inhibitor led to the replacement of inhibitor by the ions of water or chlorine thus reduce the inhibition efficiency [23].

The increase in the value of $R_t$, reduced the value of $\text{CPE}_{\text{dl}}$ due to the presence of inhibitor [21] and led to a better corrosion performance. This phenomenon related to the adsorption of molecules on the metal surface. It then led to the decrease in local dielectric constant and/or the increase of thickness of electrical double layer [25].

3.2.2. Potentiodynamic polarization

Figure 5 shows the potentiodynamic of anodic and cathodic polarization plot of bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE (figure 5(A)) and TME (figure 5(B)) in 3.5 wt% NaCl solution. The electrochemical polarization parameters such as corrosion current density ($i_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), anodic and cathodic Tafel slopes ($\beta_\alpha$ and $-\beta_\beta$), corrosion rate (CR) and percentage inhibition efficiency (% IE) are given in tables 3 and 4 in the presence of varying concentration Zn-P coated mild steel of TAE and TME respectively. All the potentiodynamic polarization parameters were calculated by Tafel extrapolation method. By using this method, the $E_{\text{corr}}$ values derived from the intersection of anodic and cathodic polarization curves [26].

According to figure 5, the incorporation of tannin extracts with Zn-P coated mild steel showed better corrosion resistance in 3.5% (wt.) NaCl solution compared to the bare mild steel. Based on tables 4 and 5, the $i_{\text{corr}}$ value of the bare mild steel was the highest at 9.347 μA cm$^{-2}$ and this indicated that the bare mild steel was more susceptible to undergo corrosion. In contrast, the presence of tannin extracts with increasing concentration improved the corrosion performance and the optimum inhibition concentration toward corrosion was at 4 g l$^{-1}$ tannin. At this concentration, both TAE and TME Zn-P coated mild steel yielded the lowest $i_{\text{corr}}$ values that are 3.463 μA cm$^{-2}$ and 2.683 μA cm$^{-2}$. The lower the $i_{\text{corr}}$ values indicated that the better resistance against the corrosion [26].

The lower the $i_{\text{corr}}$ values means that the higher the % IE. The % IE obtained for both TAE and TME Zn-P coated mild steel were at 4 g l$^{-1}$ that are 63.15% and 71.44%, respectively. The further increase in the concentration after this optimum value the inhibition efficiency decreased. These results are in a good agreement with the EIS results indicated that both of these techniques are complementary to each other. Furthermore, based on tables 3 and 4, at 4 g l$^{-1}$ TAE and TME Zn-P coated mild steel acquired the lowest corrosion rate that are 1.582 and 1.226 mpy, respectively.

Inhibition is categorized into two types that are anodic and cathodic inhibition. It can be determined from the values of $E_{\text{corr}}$, $\beta_\alpha$, $-\beta_\beta$, and $\beta_\beta$ [22]. According to figure 5(A) and table 3, there are variations in the value of anodic and cathodic Tafel slope constants ($\beta_\alpha$ and $-\beta_\beta$) observed as the addition of TAE. Moreover, the values of $E_{\text{corr}}$, of TAE Zn-P coatings shifted to negative as compared to the bare mild steel indicated that in this analysis cathodic inhibition occurred.

According to figure 5(B) and table 4, the presence of TME Zn-P coatings caused the Tafel slope constant ($\beta_\alpha$ and $-\beta_\beta$) showed random changes and the $E_{\text{corr}}$ was observed shifted in both anodic and cathodic directions as compared to bare mild steel. This phenomenon indicated that the TME Zn-P coatings affected both anodic and cathodic processes, reduced anodic dissolution of steel and cathodic hydrogen evolution [11]. This suggested that the type of inhibition was mixed type.

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3.3. Surface analyses

3.3.1. SEM/EDX analyses

Surface morphologies of the tannin Zn-P coated, Zn-P coated, and uncoated mild steel specimens were analyzed by SEM and EDX analysis. Figure 6 illustrates the SEM images of (A) blank mild steel, (B) Zn-P coated, (C) Zn-P

Table 3. Potentiodynamic polarization parameters for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE in 3.5% (wt.) NaCl solution.

| Nature of mild steel       | E_{corr} (mV) | i_{corr} (μA cm^{-2}) | β (mV dec^{-1}) | α (mV dec^{-1}) | CR (mpy) | %IE |
|----------------------------|---------------|------------------------|-----------------|-----------------|-----------|-----|
| Bare mild steel            | -522          | 9.347                  | 78.10           | 382.9           | 4.293     |      |
| Zn-P                       | -597          | 5.79                   | 66.4            | 247.4           | 2.66      | 38.04|
| Zn-P + 2 g L^{-1} TAE      | -569          | 4.618                  | 104.7           | 573.0           | 2.110     | 50.85|
| Zn-P + 4 g L^{-1} TAE      | -549          | 3.463                  | 122.5           | 466.5           | 1.582     | 63.15|
| Zn-P + 6 g L^{-1} TAE      | -597          | 4.945                  | 69.6            | 204.2           | 2.259     | 47.38|
| Zn-P + 8 g L^{-1} TAE      | -590          | 5.638                  | 74.8            | 235.9           | 2.576     | 40.02|
| Zn-P + 10 g L^{-1} TAE     | -587          | 6.739                  | 62.4            | 97.4            | 3.079     | 28.29|

Figure 5. Tafel plot for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TAE (A) and TME (B).
coated TAE and (D) Zn-P coated TME mild steel under 500 x magnification. According to figure 6(A), the surface of the blank mild steel exhibited severe corrosion of different shape spots. Based on figures 6(B)–(D), the surface of phosphate coating has finer and tiny crystals with continuous and compact structure. The presence of internal stress in Zn-P coated mild steel led to the formation of pores [27]. Due to this event the surface of the Zn-P coated, Zn-P coated TAE and Zn-P coated TME mild steel was further analyzed with 20,000 x magnification as shown in figures 7–9, respectively. The EDX point analysis was performed at the layer and pore of Zn-P coated to observe the presence of tannin sealant. Tables 5–7 show the elements composition in Zn-P coated, Zn-P coated TAE and Zn-P coated TME mild steel detected by EDX spectroscopy.

**Table 4.** Potentiodynamic polarization parameters for bare mild steel, Zn-P coated mild steel and Zn-P coated mild steel with increasing concentration of TME in 3.5% (wt.) NaCl solution.

| Nature of mild steel | $E_{corr}$ (mV) | $i_{corr}$ ($\mu$A cm$^{-2}$) | $\beta$ (mV dec$^{-1}$) | $-\beta$ (mV dec$^{-1}$) | CR (mpy) | % IE |
|----------------------|-----------------|-----------------|-----------------|-----------------|--------|-----|
| Bare mild steel      | −522            | 9.347           | 78.1            | 382.9           | 4.293  | —   |
| Zn-P                 | −597            | 5.79            | 66.4            | 247.4           | 2.66   | 38.04 |
| Zn-P + 2 g L$^{-1}$ TME | −513            | 3.310           | 90.3            | 180.9           | 1.512  | 64.78 |
| Zn-P + 4 g L$^{-1}$ TME | −508            | 2.683           | 93.9            | 147.9           | 1.226  | 71.44 |
| Zn-P + 6 g L$^{-1}$ TME | −523            | 4.135           | 33.0            | 47.0            | 1.889  | 55.0  |
| Zn-P + 8 g L$^{-1}$ TME | −572            | 4.404           | 115.0           | 187.3           | 2.012  | 53.13 |
| Zn-P + 10 g L$^{-1}$ TME | −587           | 5.342           | 65.8            | 134.4           | 2.441  | 43.14 |

**Table 5.** Elemental compositions (wt%) of Zn-P coated at the pore and coated layer.

| Nature of Zn-P coated | Elemental composition (wt%) |
|-----------------------|-----------------------------|
|                       | Fe  | O   | C   | Zn  | P   |
| Coated layer          | 5.11| 39.19| 4.8 | 38.96| 11.93|
| Pore                  | 70.36| 23.60| 0.37| 4.64 | 1.04 |

**Figure 6.** SEM images of (A) blank mild steel, (B) Zn-P coated, (C) Zn-P coated TAE and (D) Zn-P coated TME mild steel under 500 x magnification.
According to tables 5–7 the elements such as Fe, O, C, Zn and P were detected in Zn-P coated, Zn-P coated TAE and Zn-P coated TME. It was observed that the decrease of Fe contents at the Zn-P coated layer compared to the pore indicated the presence of phosphate crystal layer [28]. Moreover, the Fe content decreased with the increase in C contents at the pore is observed when Zn-P coated mild steel undergo treatment with TAE and TME. This indicated the present of carbon correspond to the tannin sealant [7]. This prove that the tannin successfully sealed at the pore of Zn-P coated mild steel and the proposed mechanism showed in figure 10.

3.3.2. Contact angle measurement

Figure 11 illustrates the contact angle measurement of water on the surface of bare mild steel, Zn-P coating, Zn-P TAE and Zn-P TME. Based on the results obtained, bare mild steel showed the lowest water contact angle that is 41.64°. The highest contact angle achieved by Zn-P coated at the value of 118.39° followed by Zn-P TME and Zn-P TAE coated at the value of 91.53° and 84.05°, respectively. The higher contact angle is due to the higher hydrophobic properties of the surface, where the decrease in the value of the contact angle is due to the increase.
in the hydrophilic properties of coating with incorporation with tannin. Surface roughness is one of the parameters that affect the contact angle. The increase of the surface roughness of hydrophobic properties, the contact angle increases whereas the increase in roughness of hydrophilic properties, reduce the contact angle [29]. The high value of water contact angle means that the resistant toward the corrosion is higher [30].

Even though water contact angle of Zn-P tannin coated was lower than Zn-P coated, the corrosion electrochemical test showed that Zn-P tannin coated provide high corrosion protection. This is the limitation of contact angle measurement as the area of contact angle study was limited to a drop of 6.5 μl of distilled water on the surface of the sample as compared to corrosion electrochemical test, the exposed area to the reaction was 3.142 cm². The bigger area of study by corrosion electrochemical test made the results obtained more accurate compared to the water contact angle measurement.

Figure 8. SEM image and EDX diagram of Zn-P coated TAE mild steel under 20,000 x magnification.
Figure 9. SEM image and EDX diagram of Zn-P coated TME mild steel under 20,000 x magnification.

Table 6. Elemental compositions (wt%) of Zn-P coated TAE at the pore and coated layer.

| Nature of Zn-P coated TAE | Elemental composition (wt%) |
|---------------------------|-----------------------------|
|                           | Fe  | O   | C   | Zn  | P   |
| Coated layer              | 9.77| 43.0 | 8.10| 30.48| 8.65|
| Pore                      | 42.85| 37.26| 6.99| 9.73 | 3.09|
Table 7. Elemental compositions (wt%) of Zn-P coated TME at the pore and coated layer.

| Nature of Zn-P coated TME | Fe  | O   | C   | Zn  | P   |
|---------------------------|-----|-----|-----|-----|-----|
| Coated layer              | 5.03| 46.03| 9.11| 29.73| 10.10|
| Pore                      | 58.28| 30.09| 2.62| 4.92 | 4.04 |

Figure 10. Proposed mechanism of tannin adhesion on exposed surface of Zn-P coated mild steel.
4. Conclusion

The incorporation of mangrove bark tannin as a sealant after Zn-P coating treatment improved the corrosion inhibition performance and found that TME gave highest inhibition efficiency than TAE. The optimum inhibition was found at 4 g L\(^{-1}\) tannin concentration. SEM/EDX surface analysis proved the growth of Zn-P crystal on the surface of mild steel led to formation of pore. However, the pore was successfully sealed through the treatment with the tannin extracts. The wettability measurement found that the Zn-P coated mild steel give the highest contact angle that is 118.39° and this is due to the higher hydrophobic properties of the surface.

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ORCID iDs

Shahadad Zainol Abidin \(\text{https://orcid.org/0000-0002-3648-8904}\)
M Hazwan Hussin \(\text{https://orcid.org/0000-0001-8204-3685}\)

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Figure 11. Images of contact angle measurements of (A) bare mild steel, (B) Zn-P coated, (C) Zn-P TME coated and (D) Zn-P TAE coated.
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