Comparative evaluations of antioxidant potentials of *Dryobalanops aromatica* tree bark extracts as green corrosion inhibitors of mild steel in hydrochloric acid

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**Abstract**

The antioxidant potential of *Dryobalanops aromatica* methanolic (ME) and water extracts (WE) tree bark was studied by reducing power and DPPH free radical scavenging capacity assays. Methanolic extract showed better antioxidant capacity than water extract and butylated hydroxytoluene standard. The effective concentration EC50 (362.7 mg DPPH eq/g for ME and 555.4 mg DPPH eq/g for WE) and antiradical power (0.0028 for ME and 0.0018 for WE) suggest that methanolic extract has higher antioxidant properties than water extract. According to potentiodynamic polarization, electrochemical impedance spectroscopy, and electrochemical noise, employed to measure the anti-corrosion properties of the *D. aromatica* tree bark extracts on mild steel in 0.5 M HCl, the water extract seems to perform slightly better than methanol extract. The calculated percentage inhibition efficiencies of the extract at the optimum concentration (1000 ppm) were; (IE = 93.66% for ME and 92.39% for WE). Adsorption process of *D. aromatica* ME and WE on mild steel surface in HCl solution followed Langmuir adsorption isotherm. The surface morphology depicts that the surface of the mild steel treated with methanol and water extracts showed improvement compared to mild steel plate treated only with 0.5 M HCl.

**1. Introduction**

Mild steel is the most commonly used metal for constructions and other industrial applications (Ji et al 2015). It is due to the low cost, ease of fabrication and availability of the metal. However, mild steel is highly prone to corrosion, especially in acidic media. Acids such as hydrochloric acid find application in industrial processes of crude oil refining, acid-prickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and other petrochemical processes (Hussin et al 2016). The use of inhibitors to protect metals against corrosion is one of the most effective, most comfortable and practicable methods. Even though the use of synthetic inhibitors is very efficient, it has many risks due to its hazardous environmental effect and strict regulations on their usage (Ostovari et al 2009). Therefore, current modern researchers have shifted focus to green corrosion inhibitors (plant-based).

Though several plant products were reported as corrosion inhibitors (Okafor et al 2010, Nofrizal et al 2012, Peres et al 2012, Kairi and Kassim, 2013, Ji et al 2015), the need to explore more plants for green corrosion inhibition can never be over-emphasized because, the corrosion cost on the world’s economy is quite vast and on the increase. For instance, the new global direct cost of corrosion is 2.5 trillion US dollars (3.4% of global product) as reported by NACE international as part of its study in 2016 (Hou et al 2017). The tree *Dryobalanops aromatica* belonging to the family Dipterocarpaceae (Wibowo et al 2012) is about 60 m tall and spreads widely...
across the tropical rainforest of Sumatra in Indonesia; Peninsular Malaysia and Borneo in Malaysia. Other names of the tree base on location include; Camphor tree, Malay camphor, Sumatra camphor or Borneo camphor. *Dryobalanops aromatica* tree is best known for its excellent quality timber 'Kapur' (Le et al 2016). Other products from the tree are camphor (a white resinous substance) and camphor oil which are both mainly sourced from the leaf and seed of the tree. The oil of camphor is used in various medicinal purposes and for preserving dead bodies (Kamariah et al 2012). The flaky natured bark of the tree was in the past used for basket weaving, walls and huts making by surrounding dwellers (Corlett and Primack, 2005).

Nowadays, the bark of *Dryobalanops aromatica* are usually left wasted after harvesting the trees. Also, due to incessant cutting down of the trees, to give way for the planting of oil palm trees (Ritonga et al 2018), only a few species remain in the forest reserve. Hence, *Dryobalanops aromatica* stands the risk of complete extinction. Camphor oil extracted from the leaves and seeds of *Dryobalanops aromatica* have been characterized and isolated by some researchers (Cheung and Wong 1972, Syah et al 2003, Kamariah et al 2012, Kuspradini et al 2016, Le et al 2016). Report on the phytochemical screening of the tree bark methanol extract reveal it contains complex mixture of phytochemicals such as; flavonoid, tannin, saponin, coumarin, cardiac glycoside (Yakubu et al 2019), but its applications are scarce. According to Wibowo et al 2011, the bark extract of *Dryobalanops aromatica* possesses some biochemical activities including; cytotoxic effect, antifungal, anti- HIV-1 and antioxidant. The antioxidant activity of plant parts is due to the presence of polyphenolic compounds (Ostovari et al 2009, Peres et al 2012). The stem bark of *Dryobalanops aromatica* is found to contain resveratrol oligomers (Ahmat et al 2014, Manshoor et al 2015, Wang and Yao 2016), which are a group of polyphenolic compounds and derivatives of stilbenes (Cichewicz and Kouzi 2002). These polyphenolic compounds possess antioxidant properties (Privat et al 2002, Li et al 2018) which makes them applicable for corrosion mitigation therefore, in this study *D. aromatica* tree bark extracts were employed as corrosion inhibitors.

To the best of our knowledge, there is no comprehensive report on the corrosion inhibition properties of *D. aromatica* tree bark extract. The objectives of the present study are to investigate the antioxidant capacity of *Dryobalanops aromatica* stem bark methanolic and water extracts and explore the extracts corrosion inhibition potential on mild steel in hydrochloric acid medium.

2. Methodology

2.1. Sample collection and preparation

Collection of fresh tree stem bark of *D. aromatica* was carried out in 2016 at the Forest Research Institute Malaysia (FRIM), Kepong Selangor. Storage of the sample with specimen voucher number KL5829 was at the herbarium of the Department of Chemistry, University Malaya, Kuala Lumpur. Milling of the air-dried tree bark sample (5 kg) was carried out and the powder (about 8 μm), macerated with methanol (98%) for three days. Prior maceration with methanol, the powdered sample was similarly extracted exhaustively with n-hexane then ethyl acetate. The methanolic solution was decanted, filtered and concentrated using rotary evaporator (model) at 50 °C. The resulting paste was freeze-dried, resulting in a dark brown crystal of the methanolic extract (dark brown). After air-drying the residue, maceration with distilled water was done to obtain the water extract powder (light brown). Subsequently, both the methanolic and water extracts obtained were used in all the analyses.

2.2. Characterization of plant extracts

2.2.1. Fourier transform infrared spectroscopy (FTIR)

The milling of crude methanol and water extracts of *D. aromatica* bark with potassium bromide, KBr (Merck, 1:20 w/w) in a crucible and pressing using cut-pressing machine gave thin transparent pellets. The pellets were analyzed using PerkinElmer 2002 Spectrophotometer (USA) at a wavelength range of 4000 to 400 cm⁻¹, 4 cm⁻¹ resolution and eight scans, which gave the FTIR spectra of the extracts (Hussin, 2010).

2.2.2. Ultraviolet—visible spectroscopy (UV-VIS)

Each of *D. aromatica* bark extract (5 mg) was dissolved with 2% methanol in distilled water and poured into 10 ml volumetric flask. The UV-VIS measurement of the solution was carried out using UV-VIS single monochromator spectrophotometer (UV 2600 Shimadzu, Kyoto, Japan). A quartz cell with an optical path length of 1.0 cm, a wavelength range of 200–400 nm and a sampling interval of 1.0 nm were employed (Antoine et al 2004).
2.3. Antioxidant assays

2.3.1. Reducing power
The reducing power assay of plant extract, according to Subramanian et al. (2014) was employed with slight modification. Standard solution of Ascorbic acid with concentrations from 20 mg ml$^{-1}$ to 100 mg ml$^{-1}$ was prepared using ethanol (98%). To 1 ml of the solution concentrations, added 2.5 ml phosphate buffer (0.2 M, pH 6.6) and potassium ferricyanide solution with water (1%. w/v). Centrifuging of the solution was at 3000 rpm for 20 min. After which 2.5 ml of the supernatant portion of the solution (upper part) mixed with 2.5 ml distilled water and 0.5 ml ferric chloride hexahydrate solution (0.1%, w/v). Fe$^{3+}$ complex detected by measuring the UV absorbance of the solution at each concentration at 700 nm. The same measurement was carried out with other standards (gallic acid, quercetin, and butylated hydroxytoluene, BHT) and both methanolic and water extracts of D. aromatica bark. All measurements were in duplicate.

2.3.2. DPPH (Diphenyl-1-picrylhydrazyl) free radical scavenging activity
According to the procedure reported by Bag et al. (2015), the DPPH free radical scavenging capacity of methanolic and water extracts of D. aromatica bark were measured with slight modification. Ascorbic acid, gallic acid, quercetin and BHT used as standards. The solution of each standard with a concentration range from 20 mg ml$^{-1}$ to 100 mg ml$^{-1}$ was prepared using methanol. To 100 µl of each concentration solution in test-tube, 3900 µl of freshly prepared DPPH added, the mixture shaken and kept in the dark for 30 min. The UV absorbance of the solutions measured at 517 nm. A similar procedure was carried out for both extracts of the plant. All measurements were in duplicate. The calibration graph plotted for each of the standards and both extracts. The freshly prepared DPPH was covered with aluminum foil and stored (refrigerated) in between measurements.

The DPPH free radical scavenging activity of the plant extracts was calculated using the equation (1);

$$\text{DPPH scavenging activity(%) = } \frac{(A_0 - A)}{A_0} \times 100$$  (1)

where $A_0$ is the absorbance of the blank sample (control) and $A$ is the absorbance of standard or extract sample solution.

2.4. Corrosion studies

2.4.1. Preparation of specimens
Mild steel plate of grade S40500 with composition: Fe = 98.42%, C = 1.15%, P = 0.01%, Na = 0.03%, Mn = 0.15%, Al = 0.06%, Si = 0.16% was cut using metal scissors into sheets of dimension 8 × 8 × 0.1 cm. The mild steel plates were first cleaned, polished and degreased with acetone. The shiny surface of the plates was achieved after successive abrasion and smoothening with SiC papers of grades; 100, 200, 400, 600, 800, 1000 and 1200 (Noirizal et al. 2012). The plates were dried with acetone and wrapped with aluminum foil and stored in a desiccator before further use.

2.4.2. Preparation of electrolyte
Hydrochloric acid (97%, AR grade) was used to prepare the solutions for the study. Solutions of the plant extracts (methanol and water) of concentrations, 10 ppm, 50 ppm, 100 ppm, 500 ppm and 1000 ppm were prepared with 0.5 M HCl, by first dissolving the extracts with 2% ethanol to enhance dissolution of the extracts (Hussin and Kassim, 2011). The solutions were then made up to mark in 50 ml volumetric flask.

2.4.3. Electrochemical measurements

2.4.3.1. Potentiodynamic polarization (PD)
Potentiodynamic polarization was measured using the conventional three-electrode system in a cylindrical Pyrex cell of capacity 50 ml and diameter 5 cm. The working electrode (WE) was the polished square-shaped mild steel plate (8 × 8 × 0.1 cm) with exposed surface area of 0.785 cm$^2$, to allow contact with the electrolyte. The counter electrode (CE) was a platinum electrode and a saturated calomel electrode was used as the reference electrode (RE). The experiment was carried out at room temperature (30 °C ± 1) using a Gamry 600 instrument (USA), at scan rate of 0.5 mV s$^{-1}$. The open-circuit potential measured for 30 min for stabilization and steady-state potential reached before the Tafel plots obtained. The potential obtained from $E_{ocp}$ values ranges from +250 to −250 mV (Hussin and Kassim, 2011). The corrosion inhibition efficiency IE (%) was calculated using the equation (2):

$$\text{IE(%) = } \frac{E_{ocp} - E_{corr}}{E_{ocp}} \times 100$$
\[
\% \text{ IE} = \frac{i_{\text{corr}(o)} - i_{\text{corr}(i)}}{i_{\text{corr}(o)}} \times 100
\]

where \(i_{\text{corr}(o)}\) and \(i_{\text{corr}(i)}\) are the corrosion current densities without and with the addition of inhibitor (plant extract), respectively.

2.4.3.2. Electrochemical impedance spectroscopy (EIS)

The Electrochemical impedance spectroscopy measurement was carried out prior to the PD measurement (due to the PD destructive nature of the mild steel surface) using the Gamry 600 instrument (USA). The \(E_{\text{ocp}}\) was first measured to achieve stability. The impedance analysis over a frequency range of 100 kHz–0.1 Hz with an ac signal amplitude perturbation of 10 mV. The data were obtained from the diameter of semi-circles of the Nyquist plots after fitting with sets of circuit models to get the best fit (Hussin and Kassim 2010).

2.4.3.3. Electrochemical noise measurement (ENM)

Electrochemical noise measurement is a non-destructive and non-intrusive technique, which monitors the fundamental changes in an electrochemically active system. Achieved by the simultaneous measurement of current and potential fluctuations caused by the spontaneous electrochemical reactions of anodic reaction (iron dissolution) and the associated cathodic reaction (hydrogen or oxygen reduction), followed by subsequent mathematical analysis of the current and potential data (Mills and Jamali, 2016). The electrochemical noise measurement was carried out using the previous conventional three-electrode. Here, the noise resistance (\(R_n\)) in the form of small fluctuations in current and potential were measured across the working electrode-electrolyte interface (Cappeln et al 2005).

2.5. Adsorption consideration

Adsorption isotherm is essential for determining the mechanism of corrosion inhibition. Langmuir adsorption isotherm is one of the most commonly used isotherms and is given by the expression (Bagga et al 2016):

\[
\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C
\]

where \(\theta\) is the degree of surface coverage, \(C\) the concentration of inhibitor in the bulk of solution, and \(K_{\text{ads}}\) the adsorption - desorption equilibrium constant.

\[(\text{slope} = 1, \text{for uniform and monolayer adsorption, whereby no lateral interaction occurs between the molecules). Equation (3) can be transformed to give equation (4)} \ (Nwabanne & Okafor, 2012),

\[
\log \frac{C}{\theta} = \log C - \log K
\]

2.6. Surface analysis

The surface morphology analysis of mild steel surface was carried out using scan electron microscope, SEM (Quanta FEG 650). The images of the specimens were taken after dipping the plates (inhibitor-in-acid-treated) for 24 h separately for ME and WE at the optimum inhibition concentration for both extracts (1000 ppm). Afterwards, the plates were dried in oven for 5 min before analysis. The elemental composition of the polished, acid-treated and inhibitor-in-acid treated mild steel specimens were also carried out using Energy dispersive x-ray spectrometer, EDX (Oxford instrument) (Akbarzadeh et al 2011).

3. Results and discussion

3.1. Characterization of plant extracts

The UV spectrum (not shown) of methanol extract showed \(\lambda_{\text{max}}\) absorption at 286 nm (8.289). Both methanol and water extract spectra gave common \(\lambda_{\text{max}}\) absorption peak at 226 nm (6.569). These \(\lambda_{\text{max}}\) absorptions were found to characterize the UV spectrum of aqueous acetone extract of Dryobalanops aromatica bark in a previous study (Wibowo et al 2011). These absorptions are due to the presence of resveratrol oligomers, which are natural polyphenolic antioxidants (Wang & Yao, 2016). Methanol extract absorption at 269 nm (8.315) is characteristic \(\lambda_{\text{max}}\) of gallic acid and water extract absorption at 255 nm (6.780) is common \(\lambda_{\text{max}}\) absorption for quercetin and catechin (Antoine et al 2004). Other remarkable \(\lambda_{\text{max}}\) absorptions of water extract are between 223 nm (8.438) – 227 nm (8.296).

The IR absorption peaks (figure 1) appearing at 3385, 2922, 1614, 1515, 1449, and 1339 cm\(^{-1}\) for methanolic extract and 3393, 2925, 1619, 1449, and 1340 cm\(^{-1}\) for water extract are similar with those reported by Wibowo et al 2011 for aqueous acetone extract of D. aromatica stem bark. The absorption bands at 3385 cm\(^{-1}\) for methanolic extract and 3393 cm\(^{-1}\) for water extract of D. aromatica bark are characteristic of Resveratrol
The presence of alkyl group is responsible for the peak at 2922 cm\(^{-1}\) for methanolic extract and 2925 cm\(^{-1}\) for water extract (Wibowo et al. 2011). The peak at 1515 cm\(^{-1}\) for methanolic extract and 1449 cm\(^{-1}\) for both extracts are due to the presence of benzene group, which is usually around 1450–1600 cm\(^{-1}\). The presence of double bond is evident from the peak at 1614 cm\(^{-1}\) for methanolic extract and 1619 cm\(^{-1}\) for water extract of *D. aromatica* stem bark.

### 3.2. Antioxidant assays

#### 3.2.1. Reducing power assay

From reducing power assay, antioxidant concentration is directly proportional to absorbance. Usually, Fe\((CN)_6^{3-}\) ions are reduced to Fe\((CN)_6^{4-}\) ions in the presence of antioxidant (from the extract). The ferric chloride added, reacts with Fe\((CN)_6^{4-}\) ions to form intense Prussian blue complex, Fe\(_4[Fe(CN)_6]_3\) which has a strong absorbance at 700 nm (Gülçin, 2010). The reducing power is a measure of the Fe\(^{2+}\) ions concentration in the complex. In figure 2 below, Ascorbic acid (AA) and Gallic acid (GA) standards show higher absorbance than the methanolic and water extracts as compared to Quercetin (QC) and Butylated hydroxytoluene (BHT).

Methanolic extract gave similar absorbance with a gallic acid standard at the lowest concentration (20 mg l\(^{-1}\)) only. Absorbances at higher concentrations for methanolic extract were like those of BHT. The methanolic extract shows a higher antioxidant capacity than water extract. The methanolic extract of *D. aromatica* bark has been previously reported to contain higher polyphenolic content than the water extract (Yakubu et al. 2019). Also, because there is a correlation between antioxidant capacity and phenolic content of plant extract (Miliauskas et al. 2004), this could explain the reason for the antioxidant capacity trend in this work.

Note: AA = Ascorbic acid; GA = Gallic acid; QC = Quercetin; Butylated hydroxytoluene; ME = Methanolic extract; WE = Water extract.
3.2.2. DPPH assay

The DPPH is a reagent used to evaluate the free radical scavenging activity of antioxidants. The assay is based on the reduction of DPPH in alcohol, usually methanol (Mishra et al 2012). In the reaction, the antioxidant scavenges the stable DPPH free radical to form a non-radical, DPPH. The evidence is the appearance of purple colour of the reaction mixture, which changes to yellow, and a decrease in the absorbance at 517 nm (Gülçin, 2010). The antioxidant activity of methanolic and water extracts of *D. aromatica* determined by DPPH radical scavenging analysis and from the percentage free radical scavenging capacity (figure 3), calculated effective concentration (EC$_{50}$) and antiradical power (table 1), the extracts are said to be effective antioxidants. While AA, GA and QC standards show higher scavenging capacity than methanolic and water extract, both extracts revealed better capacity than BHT with methanolic extract as a better scavenger of DPPH free radicals than water extract, as shown in the figure. The EC$_{50}$ is the amount of the extract needed to scavenge 50 % of the initial concentration of the free radical of DPPH while, the antiradical power is the inverse of EC$_{50}$ (Brand-Williams et al 1995). As expected, the methanolic extract of *D. aromatica* tree bark showed higher EC$_{50}$ as well as antiradical power (reciprocal of EC$_{50}$) than the water extract.

![Figure 3. Free radical scavenging capacity (% DPPH) of *D. aromatica* tree bark extracts compared to standard samples.](image)

| Parameter                  | Methanol extract | Water extract |
|----------------------------|------------------|---------------|
| Effective concentration (EC$_{50}$) | 362.7 mg DPPH eq/g | 555.4 mg DPPH eq/g |
| Antiradical power (ARP)     | 0.0028           | 0.0018        |

3.3. Corrosion studies

3.3.1. Potentiodynamic polarization

The corrosion parameters obtained from the Tafel polarization curves (figures 4(a) and (b)) extrapolation, for the corrosion of mild steel with effect of the concentrations of methanolic and water extracts of *D. aromatica* bark, in 0.5 M HCl at room temperature (≈303 K ± 2) include; corrosion potential $E_{\text{corr}}$, current density $i_{\text{corr}}$, Tafel anodic ($\beta_a$) and cathodic ($\beta_c$) slopes as given in table 2. The corrosion potential $E_{\text{corr}}$ values changed with the addition of the extracts and did not follow any pattern, indicating that the constituents of the extracts inhibited the corrosion rate in hydrochloric acid (Hussin, 2010). The corrosion current density ($i_{\text{corr}}$) values diminished with increasing concentration of inhibitors, which is required for effective corrosion inhibition (Ji et al 2015). It shows that both extracts of the tree bark retarded the corrosion rate of mild steel in hydrochloric acid.

Significant difference in the Tafel slope ($\beta_a$ and $\beta_c$) values with addition of inhibitor for both extracts when compared with that of 0.5 M HCl (blank) can be observed. Even though, changes as concentration of both inhibitor extracts was increased did not follow any trend, they indicate that the inhibitor extracts prevented the metal corrosion by controlling both metal dissolution at the anodic site and hydrogen evolution at the cathodic...
site, with the cathodic reaction been predominant (Nofrizal et al 2012). The Tafel plots appears clustered together with minimal shift from the cathodic (noble) region to the anodic (active) region can be observed. It indicates that both metal dissolution and hydrogen evolution reaction on the mild steel surface were suppressed and that methanolic and water extracts of the tree bark acted as mixed inhibitors (Ostovari et al 2009). From table 2, though the inhibition efficiency (IE) for methanolic extract is slightly higher at the optimum concentration (1000 ppm) than that of water extract, the % inhibition efficiencies at all other concentrations are

![Figure 4](image-url). Tafel plots in the absence and presence of (a) methanol extract, and (b) water extract of D. aromatica tree bark.

Table 2. The corrosion parameters of potentiodynamic polarization for methanol and water extracts.

| Sample            | $E_{corr}$ (mV) | $i_{corr}$ ($\mu$A cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $-\beta_c$ (mV dec$^{-1}$) | CR (mpy) | %IE  |
|-------------------|-----------------|-------------------------------|---------------------------|----------------------------|----------|------|
| 0.5 M HCl         | $-509.0$        | $451.0$                       | $424.5$                    | $666.3$                    |          |      |
| 10 ppm ME         | $-513.0$        | $199.0$                       | $88.20$                    | $115.7$                    | $2.353$  | $55.88$|
| 50 ppm ME         | $-496.0$        | $166.0$                       | $102.4$                    | $206.1$                    | $1.963$  | $63.19$|
| 100 ppm ME        | $-482.0$        | $117.0$                       | $62.10$                    | $173.8$                    | $1.383$  | $74.06$|
| 500 ppm ME        | $-486.0$        | $82.40$                       | $48.50$                    | $168.5$                    | $0.974$  | $81.73$|
| 1000 ppm ME       | $-490.0$        | $28.60$                       | $53.90$                    | $91.00$                    | $0.338$  | $93.66$|
| 10 ppm WE         | $-507.0$        | $170.0$                       | $110.3$                    | $109.1$                    | $2.010$  | $62.31$|
| 50 ppm WE         | $-501.0$        | $118.0$                       | $90.10$                    | $115.3$                    | $1.395$  | $73.84$|
| 100 ppm WE        | $-491.0$        | $95.70$                       | $75.60$                    | $110.5$                    | $1.132$  | $78.78$|
| 500 ppm WE        | $-438.0$        | $80.00$                       | $67.00$                    | $142.8$                    | $0.946$  | $82.26$|
| 1000 ppm WE       | $-475.0$        | $34.30$                       | $50.10$                    | $93.10$                    | $0.406$  | $92.39$|
higher for water extract than for methanol extract. The reason could be attributed to the complete solubility of water extract in the acid solution compared to methanol extract, which was partially soluble. More so, the methanolic extract precipitated (forming polymer) after standing in the acid solution for a while, and this could have affected the actual concentration of methanol extract. Therefore, 2% ethanol was initially added to the extracts before mixing with the electrolyte (0.5 M HCl) and the experiment was carried out immediately to avoid formation of precipitate.

3.3.2. Electrochemical impedance spectroscopy

Nyquist plots obtained from the EIS analysis at room temperature ($\approx 303 \text{ K} \pm 2$) without the use of water bath, is as shown in figures 5(a), and (b) for methanolic and water extracts of *D. aromatica* bark extracts respectively. A depressed semi-circle (capacitive loops) can be observed from each plot, which increased in diameter as concentrations of inhibitors increased. It indicates that a charged transfer mainly controls the corrosion process. Moreover, the inhibitive film formed with the addition of the extracts got strengthened (Hussin et al 2016). The depressed semi-circle is a characteristic of solid electrodes and often refers to the frequency dispersion that arises from the roughness and other inhomogeneities of the mild steel surface (Hussin et al 2016).

The impedance parameters, as shown in table 3, were calculated by analyzing the impedance plots using the equivalent circuit model shown in figure 6. The charge transfer resistance $R_{ct}$ or sometimes referred to as $R_{p}$, is a measure of electron transfer across the metal surface and is inversely proportional to corrosion rate $C_R$. $R_s$ or $R_u$ is the resistance of the electrolyte solution. Constant phase element CPE (figure 7) was introduced into the circuit to replace a pure double-layer capacitor to give a better fit (Nofrizal et al 2012). The reason is that a parallel network of the charge transfer resistance and double-layer capacitance ($R_{ct}$-$C_{dl}$) usually gives a sparse approximation especially, for a system with an efficient inhibitor. CPE is the irregularity of the electrode surface, which causes even more depression of the Nyquist semi-circle, where the metal-electrolyte interface acts as a capacitor with an irregular surface (Ji et al 2015). The expression of CPE given as;
\[ w = Z_{\text{CPE}} \left( j\omega \right)^{-n} \]

where \( Y_0 \) is the magnitude of CPE; \( j \) is the imaginary unit; \( \omega \) is the angular frequency (\( \omega = 2\pi f \)) (where \( f \) is the AC frequency), and ‘\( n \)’ is the CPE exponent (Phase shift).

The general unit for CPE is F cm\(^{-2}\) and it can be seen to decrease with the addition of the inhibitors while, the values of ‘\( n \)’ changed without any trend. According to equation (5), if \( n = 0 \), the electric circuit will show the characteristics of a pure resistance with a magnitude of \( Y^{-1} \), if \( n = 1 \), electric circuit will correspond to a pure capacitance with magnitude of \( C \). And for \( n = -1 \), the circuit will represent a pure inductor with magnitude of \( Y^{-1} \). These mean that an increase in the values of ‘\( n \)’ shows capacitive behaviour of the mild steel in HCl solution in the presence of the extracts. However, in this case, ideal capacitor behaviour was not observed (\( n < 1 \)), which could have resulted from the irregularity of the surface of the working electrode (mild steel) or the arbitrary distribution of current on the electrode surface causing frequency dispersion (Peres et al 2012).

At the optimum concentration (1000 ppm) both extracts showed almost equal % inhibition efficiencies with water extract having slightly higher antioxidant capacity than methanol extract. It could be due to the complete solubility of water extract in the acid solution compared to methanol extract which was not completely soluble, and this could have altered the actual concentrations of methanolic extract.

It could be observed that % IE of PD and EIS analyses for both inhibitor extracts vary slightly. This could be due to the difference in the time taken for each analysis to be completed. In the sequence analyses performed, the time taken to complete one round of PD analysis was twice that of EIS analysis. There is usually an increase in corrosion resistance of the mild steel for inhibited solutions with longer immersion time (Peres et al 2012). This could explain why % IE was higher for PD than for EIS measurement with both inhibitor extracts of \( D. \) aromatica.

3.3.3. Electrochemical noise

Electrochemical noise, EN gives information about the electrochemical noise resistance (\( R_n \)), which is one of the most critical parameters of a corroding system. To calculate \( R_n \), divide the standard deviation of potential noise (\( \sigma_\alpha \)) by the standard deviation of current noise (\( \sigma_i \)) (Mills and Jamali, 2016). EN is an effective electrochemical technique due to its simplicity, relatively quick measurement and inexpensive instrumentation and so ideal for in-situ corrosion measurement (Kearns et al 1996).

The current noise, as shown in figure 7(a) and the potential noise in figure 7(b), appear to be similarly minimal for methanolic and water extracts as compared with the blank, which has more noise. The overlapping of signals of both extracts for current noise and potential noise could imply that both extracts showed about the

![Figure 6. The Randle’s CPE equivalent circuit model.](image-url)

Table 3. The impedance parameters of EIS for methanol and water extracts.

| Sample      | \( R_p \) (\( \Omega \) cm\(^2\)) | \( R_u \) (\( \Omega \) cm\(^2\)) | \( CPE (\mu \text{cm}^{-2}) \) | \( n \) | % IE  |
|-------------|--------------------------------|---------------------------------|-------------------------------|-----|-----|
| 0.5 M HCl   | 95.15                         | 4.315                           | 193.00                        | 0.8145 | —   |
| 10 ppm ME   | 223.5                         | 3.219                           | 155.20                        | 0.8432 | 57.43 |
| 50 ppm ME   | 254.0                         | 4.221                           | 112.20                        | 0.8655 | 62.54 |
| 100 ppm ME  | 274.9                         | 3.162                           | 103.80                        | 0.8538 | 65.39 |
| 500 ppm ME  | 298.2                         | 3.303                           | 82.09                         | 0.9208 | 68.09 |
| 1000 ppm ME | 465.6                         | 3.509                           | 49.30                         | 0.8732 | 79.57 |
| 10 ppm WE   | 241.1                         | 3.579                           | 132.90                        | 0.827 | 60.52 |
| 50 ppm WE   | 307.9                         | 3.012                           | 107.40                        | 0.8343 | 69.10 |
| 100 ppm WE  | 331.4                         | 3.002                           | 106.10                        | 0.8576 | 71.29 |
| 500 ppm WE  | 424.0                         | 3.128                           | 99.14                         | 0.8835 | 77.56 |
| 1000 ppm WE | 458.1                         | 3.577                           | 82.09                         | 0.9208 | 80.48 |
same resistance to the flow of current, which favored the inhibition process. The inhibition efficiencies of this technique, as shown in table 4, were less than that obtained from PD and EIS techniques. The differences in the % IE could be due to the different experimental procedures (Hussin, 2010). Though, the % inhibition efficiencies of both extracts for EN techniques appears to be lower than that obtained using PD and EIS, both extracts the performed almost similarly in the three methods. It could be due to the similarity in the polarity of methanol and water polarity (Quraishi et al 2010).

3.4. Adsorption isotherms and inhibition mechanism

The degree of surface coverage, $\theta$ was computed for the different concentrations for both inhibitors (ME and WE) from PD and EIS measurements using (Nofrizal et al 2012);

$$\theta = \frac{IE}{100}$$

Assuming there is direct relationship between the surface coverage and inhibition efficiency (IE). The values of surface coverage obtained were applied to various adsorption isotherm models, the linearity of the plot and goodness of coefficient correlation ($R^2$) were taken as indication that the experimental data for the studied

| Samples                        | $R_n$ | % IE  |
|-------------------------------|-------|-------|
| Blank (0.5 M HCl)             | 8.586 | —     |
| Methanolic extract            | 27.04 | 68.25 |
| Water extract                 | 27.69 | 68.99 |

Figure 7. Comparative (a) current noise, and (b) potential noise spectra for methanol and water extracts of D. aromatica tree bark.
inhibitor obeys a specific adsorption isotherm. Langmuir adsorption isotherm plot of log $C/\theta$ versus log $C$ as shown in figures 8 and 9 and the parameters are as presented in table 5. The closeness of $R^2$ values to unity indicates strong adherence to Langmuir isotherm (Nwabanne and Okafor, 2012). While the Langmuir isotherm postulates monolayer adsorption of the inhibitor on the metal surface and does not account for molecular interaction between the adsorbed species, the slope values as given in table 5 are slightly greater than unity. The deviation from unity implies that there is interaction between adsorbed species on the metal surface and so the Langmuir adsorption isotherm does not strictly apply (Odewunmi et al. 2015). And this is expected, given the fact that $D. aromatica$ ME and WE are composed of different organic compounds which can interact through mutual repulsion or attraction (Ekanem et al. 2010). Therefore, some components of the extracts can be adsorbed on both anodic and cathodic sites, resulting in the deviation from unit gradient. The equilibrium constant for adsorption-desorption process ($K_{ads}$) values as shown in table 5 were intercept estimations of Langmuir isotherm plot and used to calculate the standard Gibb’s free energy ($\Delta G_{ads}$) of the adsorption process based on the relationship (Kamal and Sethuraman, 2012):

$$\Delta G_{ads} = -RT \ln (A \times K_{ads})$$

where $R$ is the general gas constant (8.3142 JK$^{-1}$ mol$^{-1}$); $T$ is the Kelvin temperature (303 K); $A$ is the molar concentration of water (55.5 M or 1000 g l$^{-1}$) and $K_{ads}$ is the equilibrium constant.

The values of the free Gibb’s energy $\Delta G_{ads}$ are negative and around $-20$ KJmol$^{-1}$, which describes that the adsorption process is more towards physiosorption or physical adsorption. Physiosorption interaction occurs with addition of the inhibitor onto the metal surface due to electrostatic interactions (weak Van der Waals interaction) between the inhibitor molecules and the charged mild steel surface or inhibitor- solvent interactions (hydrophobic). While the values of $\Delta G_{ads}$ if $-40$ KJmol$^{-1}$ or more negative, involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond and indicates chemical adsorption or chemisorption (Yaro et al. 2013).

The adsorption process of organic inhibitor molecules at the metal-solution interface is very important step in the inhibition of metallic corrosion in acidic solution. The adsorption dependence on the chemical composition of the inhibitor molecules, temperature and electrochemical potential at the metal-solution interface...
In the process, the adsorbed molecules are removed from the surface in a displacement reaction. Equation of the process is given as \( \text{Org}_{\text{sol}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{Org}_{\text{ads}} + n\text{H}_2\text{O}_{\text{sol}} \) \( \text{Quraishi et al. 2010} \), where 'n' is the coefficient which represents number of water molecules that is replaced by a unit of organic inhibitor. The metal surface in aqueous solution is usually covered with adsorbed water dipoles, hence the adsorption of inhibitor molecules from aqueous solution could be described as a quasi-substitution process between the organic compound in the aqueous phase \([\text{Org}_{\text{sol}}]\) and water molecule at the electrode (mild steel) surface \([\text{H}_2\text{O}_{\text{ads}}]\) \( \text{Ekanem et al. 2010} \).

### 3.5. Surface analysis

SEM image of polished mild steel (figure 10(a)) is comparable with acid-treated (figure 10(b)), 1000 ppm ME (figure 10(c)) and WE (figure 10(d)) treated mild steel plates. The improved mild steel surfaces of ME and WE treated plates could suggest that the phytochemical constituents of the extracts were adsorbed on the surfaces of

### Table 5. Langmuir adsorption isotherm parameters.

| Data | Extract | Slope | \( R^2 \) | \( K_{\text{ads}} \) | \( \Delta G_{\text{ads}} \) (kJmol\(^{-1}\)) |
|------|---------|-------|---------|--------------|-------------------|
| PD   | ME      | 1.1222| 0.9995  | 22.57        | −25.25            |
|      | WE      | 1.0829| 0.9996  | 22.21        | −22.22            |
| EIS  | ME      | 1.0653| 0.9994  | 7.687        | −7.657            |
|      | WE      | 1.0637| 0.9999  | 10.35        | −10.35            |
the mild steel plates (Ostovari et al. 2009) thereby, forming a protective layer which minimized the attack of aggressive Cl$^-$ ions from the HCl solution which corroded the surface of the acid-treated plate (blank). The SEM micrographs show that WE treated mild steel was substantially inhibited from the effect of the acid compared to the ME treated plate.

The quantity of elements on the surface area of the mild steels were also measured before and after treatment with acid and both extracts using EDX analysis. The EDX spectra show variations in the quantity of Fe, C, O and Cl on the surface of each plate, as given in table 6. The polished plate surface (figure 10(a)) shows higher Fe content, lower O and absence of Cl compared to the acid treated plate (figure 10(b)) which shows higher O and Cl content due to corrosion.

Figure 10. EDX spectra and SEM images (at 500x magnification) of (a) a polished mild steel plate, (b) blank, (c) ME, and (d) WE of Dryobalanops aromatica tree bark.
Table 6. Elemental composition of mild steel plate before and after treatment.

| Sample                                      | Elemental composition (weight%) |
|---------------------------------------------|--------------------------------|
| Methanol extract treated plate              | C  O  Cl  Fe                   |
| Water extract treated plate                 | 8.60  4.41  —  86.99           |
| Bare mild steel plate                       | 8.68  5.32  —  85.99           |
| Blank (0.5 M HCl treated) mild steel plate  | 2.41  2.26  —  95.33           |
| ME                                          | 1.83  34.38  1.89  61.91       |
| WE                                          | —  —  —  —                          |

The spectra of ME and WE treated plates (figures 10(c) and (d)) show higher Fe and C and lower O and Cl due to corrosion inhibition compared with the acid-treated mild steel surface. These suggest that a protective film formed from adsorbed tree bark extract constituents which could have increased the carbon content and aided the inhibition process (Kairi and Kassim, 2013), where WE performed better than ME.

4. Conclusion

The studies revealed that Dryobalanops aromatica tree bark methanol extract, ME exhibited higher antioxidant capacities than the water extract, WE. While the inhibition efficiency of WE were found to be slightly higher than the ME, which makes WE a better inhibitor of mild steel corrosion in hydrochloric acid than ME. These imply that Camphor tree bark 'waste' could now be considered as useful natural resource in corrosion mitigation application.

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