**Article**

**Pitting Potential Improvement of 304 Stainless Steel in Hydrochloric Acid Solution by *Terminalia bellirica* Fruit Extract**

Sutha Sutthiruangwong *, Chutikan Wongpaiboon, Nathatida Sritha and Nattha Anukulkich

Department of Chemistry, School of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand
* Correspondence: sutha.su@kmitl.ac.th

**Abstract:** Pitting is a form of localized corrosion. One way to increase pitting resistance is, therefore, to cover surfaces with inhibitor molecules. Many plant extracts have been reported to be able to adsorb onto metal surfaces. According to uniform corrosion, the corrosion rate is reported to be decreased due to adsorption. *Terminalia bellirica* fruit contains organic chemicals which can adsorb onto metal surfaces. The extract of *Terminalia bellirica* fruit was used in this work as a corrosion inhibitor for 304 stainless steel in an acidic solution. The results showed a decrease in the corrosion current density of 304 stainless steel when the extract was added. A very high corrosion inhibition efficiency (%IE) of 95% was obtained with an extract addition of 300 mg L\(^{-1}\). Moreover, *Terminalia bellirica* fruit extract clearly showed an increase in the pitting potential of 304 stainless steel in potentiodynamic polarization curves, which was caused by the physical adsorption. The Langmuir adsorption isotherm model can be used to describe the adsorption of the extract molecule on 304 stainless steel surfaces. Besides the conventional pitting potential (\(E_{\text{pit}}\)), the parameter called pitting potential improvement in percentage (%PPI) was shown in this work. Additionally, it was calculated based on two boundaries. It can be used to quantify the pitting potential in a percentage. Pitting resistance both in terms of pitting potential and in terms of pitting potential improvement was found to be increased with increasing concentrations of the extract. The highest pitting potential improvement of 29% was achieved at 300 mg L\(^{-1}\) of extraction addition.

**Keywords:** pitting; pitting potential; corrosion; stainless steel; *Terminalia bellirica*

**1. Introduction**

*Terminalia bellirica* can be found in tropical forests in many parts of Asia. Its grilled fruits are used as an effective cure for diarrhea [1]. Its fruit extract is also a potential source for developing broad-spectrum antibacterial drugs against multidrug-resistant bacteria [2]. Its ethyl acetate fraction from ethanolic extract has long been used in liver diseases [3]. Green chemicals are nowadays interesting to many researchers including corrosion inhibition [4–6]. The corrosion inhibitions of stainless steel by herbal extracts, especially in terms of pitting inhibition, are studied by some researchers. An increase in corrosion inhibition is obtained by the formation of a protective layer. [7–10]. By the substitution of synthesis chemicals with green chemicals from nature, many advantages including lower cost, abundance, and environmental friendliness can be achieved.

Pitting is one of the most common forms of corrosion and occurs on passive metals such as stainless steel. Pitting is a form of localized corrosion. It occurs when a distinct anodic site is established. Additionally, the active dissolution is dominated and surrounded by a passivated cathodic zone. This results in the formation of an active pit on the metal surface [11]. One way to increase pitting resistance is, therefore, to cover the passive surface with adsorbed inhibitor molecules to increase the anodic-to-cathodic area ratio. Once the cathodic zone is covered by an inhibitor, the active cathodic area is decreased. A small anode or large cathode configuration is dangerous for the corrosion process. A small anode
accelerates the localized corrosion process because the current intensity on the anodic site is forced to be very high to supply an adequate number of electrons to the adjacent large cathodic zone. Environmental parameters as well as the metal compositions are reported to have an influence on the pitting potential of stainless steel in a chloride-containing medium. Equivalent number (PREN) is correlated to the likelihood of pitting occurrence [12]. Surface finishing is also reported to influence the corrosion resistance of stainless steel [13]. The fine-grained microstructure exhibits inferior pitting resistance due to its higher random high-angle boundary surface area which serves as a preferential site for the nucleation and growth of pits [14]. A study on the pitting behavior of stainless steel in HCl solutions at different pH shows that uniform corrosion occurs at pH < 1.5, whereas pitting occurs at 2.25 ≤ pH ≤ 4.25 [15]. One of the possible mechanisms for pit initiation is the penetration mechanism. In this mechanism, aggressive anions are transported through the oxide film to the underlying metal surface where they participate in localized dissolution at the metal–oxide interface [16]. Therefore, any extra organic or inorganic layer on top of the oxide film should be able to lower this penetration and yield an improvement in pitting resistance.

Many plant extracts have been reported to be able to adsorb onto metal surfaces. The uniform corrosion rate is found to decrease in both acidic and basic solutions [17–19]. The comparison of the corrosion rate between with and without inhibitor addition is generally made using corrosion inhibition efficiency percentage (IE). The formula is effective and straightforward. The corrosion rate obtained from a metal sample in the solution without inhibition is considered to be 0%IE. The decreased corrosion current density after inhibitor addition yields an increase in %IE [20–23]. In the case of localized corrosion such as pitting, the calculation of %IE which is derived from a uniform corrosion viewpoint using corrosion current density may not provide information about pitting. Pitting potential (\(E_{\text{pit}}\)) is then conventionally used to quantify the pitting resistance. The higher the pitting potential, the higher the pitting resistance of the material [24,25]. However, there can be another approach to quantify the pitting behavior in percentage. This work aims to show a parameter called pitting potential improvement in percentage (%PPI) based on the calculation using two boundaries which are from the potentiodynamic polarization data of 304 stainless steel from the absence and the presence of \(Terminalia bellirica\) fruit extract. The surface adsorption, corrosion inhibition efficiency, and pitting resistance of 304 stainless steel can be improved by the addition of the \(Terminalia bellirica\) fruit extract.

2. Experimental

2.1. Preparation of 304 Stainless Steel Samples

A type 304 stainless steel sheet (the standard chemical composition according to AISI is listed in Table 1) was cut, and samples with a circular shape 1.6 cm in diameter were obtained. After that, the sample was firstly ground in the presence of water using abrasive paper number 280. Then, the abrasive papers, numbers 600, 1200, and 2000, were applied consecutively. The 304 stainless steel sample was cleaned and then immersed in a 44 kHz ultrasonic bath with ethanol for 2 min. Finally, the sample as shown in Figure 1 was dried with hot air prior to any further electrochemical measurements.

![Figure 1. Type 304 stainless steel sample in a circular shape.](image)
2.2. Preparation of Terminalia bellirica Fruit Extract

The extract preparation is shown in Figure 2. *Terminalia bellirica* fruits were collected and cleaned with water. They were later dried and ground into powder. Then, the fruit powder was weighed to obtain 100 g and mixed with absolute ethanol to 1000 mL. The obtained solution was kept at room temperature for 3 d. After that, the solution was sent to vacuum filtration. The filtrate was evaporated with a rotary evaporator at 65 °C. After 5 h, the extract was finally obtained and stored in a dark bottle.

![Extract Preparation](image)

**Figure 2.** Preparation of *Terminalia bellirica* fruit extract.

2.3. Corrosion Testing

2.3.1. Potentiodynamic Polarization

The 3-electrode corrosion cell was applied at 25 °C in this study. The Autolab PG-STAT302N potentiostat/galvanostat with the current range of 1 A to 10 nA was used. The working electrode was a ground circle of 304 stainless steel. It was installed in a sample holder with a polytetrafluoroethylene (PTFE) gasket to maintain the exposure area of 1 cm². The reference electrode was a saturated calomel electrode (SCE) with a potential difference of 0.241 V versus a standard hydrogen electrode (SHE). Therefore, all potentials reported in this work are based on the potential of saturated calomel electrodes. The reference electrode was connected to the system by a Luggin capillary. The tip of the capillary was placed next to the surface of the working electrode at a distance of approximately 2 mm. A platinum plate was applied as a counter electrode.

Hydrochloric acid was used to prepare a pH 2.30 solution using deionized water and a calibrated pH meter. The concentration of chloride ions according to this pH is about 177 mg L⁻¹. In the case of the corrosion inhibition study, the extract was added to the testing solution at concentrations of 10, 100, 300, and 400 mg L⁻¹. The testing solution of 600 mL was purged with nitrogen 30 min prior and during the potentiodynamic polarization at a flowrate of 2.0 L min⁻¹ to reduce the oxygen levels. After the immersion of a working electrode in the testing solution, the open circuit potential (OCP) was measured. The potential was then forced into the cathodic region with respect to the OCP. Then, the potential was controlled to increase toward noble potential. The scan rate was adjusted to 0.600 V h⁻¹. At the end of the scan, the potential went back to the OCP and the potentiodynamic polarization curve was obtained. The versatile Tafel extrapolation technique was
applied to the curve for corrosion potential and corrosion current density determination. It was performed at about $E_{corr}$ by using the first linear portion of the cathodic part (on the left-hand side of $E_{corr}$) and the first linear portion of the anodic part (on the right-hand side of $E_{corr}$). Pitting potential was determined according to a sharp increase in current density next to the observed passive region.

2.3.2. Scanning Electron Microscopy

The scanning electron microscope was applied after chronoamperometry. The experimental setup for the working, reference, and counter electrode was the same as described in the potentiodynamic polarization. The potential of 0.100 $V_{SCE}$ was applied right after the immersion of the working electrode for 5 min. The surface of the sample was then investigated using a Carl Zeiss EVO MA 10 scanning electron microscope.

2.4. Fourier-Transform Infrared Spectrophotometric Measurements

The extract was prepared and analyzed by a high-sensitivity SHIMADZU IRTracer–100 for the responsible functional group in corrosion inhibition. In addition, the 304 stainless steel sample after being immersed in hydrochloric acid solution with 300 mg L$^{-1}$ extract concentration was analyzed by using a Bruker Tensor 27 FTIR with Hyperion 3000 FPA microscope with a resolution of 4 cm$^{-1}$ and 64 scans. The spectra were recorded in the range of 4000 to 600 cm$^{-1}$.

3. Results and Discussion

3.1. Potentiodynamic Polarization

Figure 3 shows the potentiodynamic polarization curves of 304 stainless steel in hydrochloric acid solution with different concentrations of $Terminalia bellirica$ fruit extract. The electrochemical parameters obtained from the polarization curves are shown in Table 2. The corrosion potentials ($E_{corr}$) of all samples were in a narrow range at about $-0.365 V_{SCE}$.

![Figure 3](image_url)  
**Figure 3.** Potentiodynamic polarization curves of 304 stainless steel in hydrochloric acid solution with and without the addition of $Terminalia bellirica$ fruit extract.
Table 2. Corrosion parameters of 304 stainless steel in hydrochloric acid solution with and without the addition of *Terminalia bellirica* fruit extract.

<table>
<thead>
<tr>
<th>Extract Concentration (mg L(^{-1}))</th>
<th>pH of the Solution</th>
<th>(E_{\text{corr}}) (V(_{\text{SCE}}))</th>
<th>(i_{\text{corr}}) (A cm(^{-2}))</th>
<th>(E_{\text{pit}}) (V(_{\text{SCE}}))</th>
<th>%IE</th>
<th>%PPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.30</td>
<td>−0.387</td>
<td>(7.90 \times 10^{-6})</td>
<td>0.027</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>10</td>
<td>2.30</td>
<td>−0.331</td>
<td>(7.51 \times 10^{-7})</td>
<td>0.126</td>
<td>90</td>
<td>12</td>
</tr>
<tr>
<td>100</td>
<td>2.29</td>
<td>−0.334</td>
<td>(7.76 \times 10^{-7})</td>
<td>0.156</td>
<td>90</td>
<td>16</td>
</tr>
<tr>
<td>300</td>
<td>2.28</td>
<td>−0.372</td>
<td>(4.17 \times 10^{-7})</td>
<td>0.263</td>
<td>95</td>
<td>29</td>
</tr>
<tr>
<td>400</td>
<td>2.28</td>
<td>−0.401</td>
<td>(4.91 \times 10^{-7})</td>
<td>0.251</td>
<td>94</td>
<td>27</td>
</tr>
</tbody>
</table>

According to the potentiodynamic polarization curve of the sample without extract addition in Figure 3, the active–passive transition can clearly be seen at the nose of the curve at about −0.346 V. The \(E_{\text{corr}}\) of this stainless steel sample was at a low value of −0.387 V. This indicated the active condition of the sample due to the absence of oxygen in the solution.

The corrosion current density of the sample without the extract addition showed the highest value of \(7.90 \times 10^{-6}\) A cm\(^{-2}\). The corrosion current densities of the sample immersed in the hydrochloric acid solution with the extract addition were lower than the corrosion current density obtained without the extract addition by about one order of magnitude. In the case of the 10 and 100 mg L\(^{-1}\) extract concentrations, the corrosion current densities were almost the same. As the extract concentration was increased to 300 mg L\(^{-1}\), the corrosion current density was decreased to \(4.17 \times 10^{-7}\) A cm\(^{-2}\). Additionally, when the extract concentration was increased to 400 mg L\(^{-1}\), the corrosion current density was not further decreased but stayed close to the value obtained from the 300 mg L\(^{-1}\) extract concentration in the range of \(4 \times 10^{-7}\) A cm\(^{-2}\). The corrosion inhibition efficiency (%IE) was calculated using Equation (1), where \(i_{\text{corr(inh)}}\) and \(i_{\text{corr(blank)}}\) correspond to the corrosion current density of the sample with and without the *Terminalia bellirica* fruit extract addition, respectively. The very high corrosion inhibition efficiency of 95 and 94% can be obtained from the extract concentration of 300 and 400 mg L\(^{-1}\). These findings showed that the *Terminalia bellirica* fruit extract can be used as a corrosion inhibitor for 304 stainless steel in a hydrochloric acid solution.

The current density in the passive region of the sample with the *Terminalia bellirica* fruit extract addition was lower than that obtained from the sample without addition. The lowest passive current density of \(4.10 \times 10^{-7}\) A cm\(^{-2}\) was obtained from the sample with 300 mg L\(^{-1}\) extract concentration. This means the *Terminalia bellirica* fruit extract increased the stability of the passive layer.

As can be seen from the current densities in Figure 3, there was a trend of a decrease in the cathodic current density when the extract concentration was increased. This suggested that the extract was working as a cathodic inhibitor by inhibiting the cathodic process. On the other side, the current density in the anodic part was also decreased with increasing extract concentration. The current densities in the passive region obtained from the samples with extract addition were much lower than that obtained from the sample without extract addition. The pitting potentials from the samples with extract addition were also higher when compared to the pitting potential obtained from the sample without extract addition. These indicate an anodic inhibitor type. Therefore, the *Terminalia bellirica* fruit extract can be considered a mixed inhibitor.

\[
%IE = (1 - (i_{\text{corr(inh)}}/i_{\text{corr(blank)}})) \times 100
\]  

The corrosion current density decreased after extract addition because the extract molecules help to protect the 304 stainless steel surface from uniform corrosion. The highest corrosion inhibition efficiency of 95% was obtained from the 300 mg L\(^{-1}\) extract concentration. Type 304 stainless steel clearly showed passive behavior in the hydrochloric acid solution. Many organic compounds including phenolic compounds such as gallic
acid can be found in the *Terminalia bellirica* fruit [26–28]. The chemical structure of gallic acid is presented in Figure 4. Gallic acid is found to provide corrosion inhibition to carbon steel [29]. Compared to the 95% corrosion inhibition efficiency of the extract in the acidic solution in this work, the corrosion inhibition efficiency of gallic acid on mild steel at pH 7 or in a neutral solution has been reported to be about 99% [30]. In an acidic solution, the gallic acid concentration of 900 mg L\(^{-1}\) gives a corrosion inhibition efficiency of 63% for mild steel [31]. Lone pair orbitals of organic molecules are found to be stabilized on several metal surfaces, including Fe and Ni. The extract molecules with several lone pair electrons can therefore adsorb onto metal surfaces [32]. After adsorption, the extract molecules help to protect the stainless steel surface. The extract molecules adsorbed onto the natural passive layer are clear obstructions. The proton from acid dissociation has more difficulty reaching the surface of 304 stainless steel. Chloride ions are normally able to penetrate the passive layer due to their high diffusivity [33]. However, with the adsorbed obstruction, the diffusion can be inhibited. Therefore, the corrosion reaction was inhibited, and the corrosion current density decreased with the extract addition.

![Chemical structure of gallic acid.](image.png)

Figure 4. Chemical structure of gallic acid.

To confirm that the reduction in corrosion current density was not from the acid–base neutralization or the elimination of the corrosive proton due to the reaction between the extract molecules and the hydrochloric acid, the pH of the solution was measured using a calibrated pH meter. The accuracy of the pH meter is ±0.01 of the measured value. The pH of the hydrochloric acid solution without extract addition was 2.30, whereas the solution with the extract addition gave a pH value of 2.28 to 2.30. The pH of the solution was not significantly changed when the *Terminalia bellirica* fruit extract was added. If the neutralization occurred, the pH value of the hydrochloric acid solution should have been increased due to the loss of proton concentration after the acid–base neutralization. According to this pH measurement, it can be concluded that the decrease in the corrosion current density was not from the acid–base neutralization but can be from the adsorption of extract molecules onto the 304 stainless steel surface.

3.2. *Terminalia bellirica* Fruit Extract Adsorption

Fourier-transform infrared spectrophotometric measurements (FT–IR) have been used to obtain possible interaction between extract molecules and 304 stainless steel surfaces in hydrochloric acid solution. Figure 5 shows FT–IR spectra of the *Terminalia bellirica* fruit extract and the adsorbed layer of the extract on 304 stainless steel.
The characteristic infrared bands of organic molecules found in the literature were used as references [34]. The FT-IR spectrum of the *Terminalia bellirica* fruit extract (Figure 5a) showed the peak for O–H stretching (carboxylic acid) at 3240 cm\(^{-1}\), C–H stretching (aromatic) at 3007 cm\(^{-1}\), C–H stretching (aliphatic) at 2922 and 2853 cm\(^{-1}\), C=O stretching (ester) at 1741 cm\(^{-1}\), C=O stretching (carboxylic acid) at 1708 cm\(^{-1}\), C=C stretching (aromatic) at 1610 and 1456 cm\(^{-1}\), and C–O stretching at 1166 and 1029 cm\(^{-1}\). The FT-IR spectrum of the adsorbed layer of the extract on 304 stainless steel is shown in Figure 5b. It was found that the peak for C–H stretching (aromatic) shifted from 3007 to 3006 cm\(^{-1}\), and C–H stretching (aliphatic) shifted from 2922 and 2853 cm\(^{-1}\) to 2918 and 2850 cm\(^{-1}\). The peak for C=O stretching (carboxylic acid) shifted from 1708 to 1693 cm\(^{-1}\), C=C stretching (aromatic) shifted from 1456 to 1444 cm\(^{-1}\), and C–O stretching shifted from 1166 and 1029 cm\(^{-1}\) to 1163 and 1055 cm\(^{-1}\). These progressive shifts in the wavenumber indicated interactions between the extract and the 304 stainless steel surface. The shift in wavenumber from 1708 to 1693 cm\(^{-1}\) of the stretching vibration of C=O (carboxylic acid) suggested that this functional group of the extract molecules, e.g., gallic acid, may be adsorbed onto the 304 stainless steel surface.

Adsorption isotherm studies can give information on how the extract molecules adsorb onto the metallic surface [35–38]. The Langmuir adsorption isotherm model (Equation (2)) was applied in this study to describe the adsorption mechanism of the *Terminalia bellirica* fruit extract on the 304 stainless steel surface. \( C \) is the extract concentration. \( \theta \) is the fractional surface coverage (%IE/100). Additionally, \( K_{\text{ads}} \) is the adsorption equilibrium constant.

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

Figure 6 shows the plot between \( C / \theta \) and \( C \). By applying linear regression, the correlation coefficient \((R^2)\) was 0.9998 which indicated a good linear relationship between \( C / \theta \)
and C. The slope of 1.05 was very close to 1. The intercept from this linear relationship was 2.36. The $K_{ads}$ can be calculated from this intercept, and the value was 0.424. The $K_{ads}$ can be used to determine Gibb’s free energy change of adsorption ($\Delta G^{\circ}_{ads}$) according to Equation (3), where $R$ is the gas constant and $T$ is the absolute temperature in Kelvin. Additionally, 55.5 represents the molar concentration of water in the solution.

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5 K_{ads})$$

![Figure 6. Plot of the Langmuir adsorption isotherm of Terminalia bellirica fruit extract on 304 stainless steel surface.](image)

The $\Delta G^{\circ}_{ads}$ for the extract adsorption on the 304 stainless steel surface was $-7.83 \text{ kJ mol}^{-1}$. The adsorption process was spontaneous. Additionally, it is well known that values of $\Delta G^{\circ}_{ads}$ of $-20 \text{ kJ mol}^{-1}$ and less negative indicate physical adsorption, whereas those of order of $-40 \text{ kJ mol}^{-1}$ or more negative indicate chemical adsorption [37]. Therefore, the adsorption of the Terminalia bellirica fruit extract on 304 stainless steel was a physical adsorption that followed the Langmuir adsorption isotherm model, indicating monolayer coverage of the extract molecules.

3.3. Pitting Potential Improvement

The pitting potentials ($E_{pit}$) of 304 stainless steel samples were shown in Table 2. The pitting potential was increased after the addition of the Terminalia bellirica fruit extract. The pitting potential of 304 stainless steel without extract addition was 0.027 $V_{SCE}$. This value was increased to 0.126 $V_{SCE}$ according to the measurement in solution with 10 mg L$^{-1}$ extract concentration. The highest pitting potential of 0.263 $V_{SCE}$ was obtained from the corrosion measurement with a 300 mg L$^{-1}$ extract concentration.

The shift of the pitting potential to a more positive value indicated a higher pitting resistance. The adsorbed extract molecules prolonged the breakdown of the passive layer. Pitting is first initiated by localized passive layer breakdown. This initiation refers to bulk metal inhomogeneity such as inclusions, dislocation, and grain boundaries as well as to passive layer properties such as local compositions and structure variations. The distinct anodic sites on the layer can be identified, and the dissolution dominates. These sites are surrounded by a passivated cathodic zone or reduction reaction. On the other hand, the weaker passive site on the 304 stainless steel surface tends to be more vulnerable to passive layer breakdown when compared to the stronger adjacent site [11,33]. The adsorbed extract molecules can cover the passive layer. The covering molecules prevent all
kinds of aggressive media, such as chloride ions and other oxidizing agents, from reaching the stainless steel surface. If the weaker site is covered by the extract molecules, the pit initiation on that particular site can be hardly initiated. In the case of an exposed weaker site (not covered by the extract molecules), this site can be prone to passive breakdown. However, the adjacent site was already covered by the extract molecules. Hence, the cathodic surface area was decreased. The ratio between anodic to cathodic surface areas was then increased. Consequently, the current intensity on the anodic site was lowered. Therefore, the probability to obtain pit initiation and pit growth was lowered when the extract molecules were adsorbed on the passive layer.

Pitting potential is a parameter for pitting resistance evaluation. When two alloys are separately immersed in the same solution, the alloy that shows the higher pitting potential will be stated as the material with the higher pitting resistance. In the case of several alloys with the same composition immersed in different solutions, the higher pitting potential means higher pitting resistance as well. An improvement in pitting potential to more positive values indicates a higher pitting resistance of the material. However, there can be another way to compare the pitting potential obtained from different extract concentrations. Passive alloys such as stainless steel exhibit pitting potentials at certain values in acidic environments [39]. Some other alloys may show only pseudopassive behavior and yield to transpassive potential instead of pitting potential [40]. In this work, the pitting potential of 304 stainless steel in a hydrochloric acid solution without extract addition was 0.027 V_{SCE}. This can be considered as a lower boundary because no lower pitting potential can be obtained in this particular acidic medium for the same material. The extract molecule from *Terminalia bellirica* fruit that has been added to the acidic medium does not decrease the pitting potential as long as it performs itself as an inhibitor. The pitting potential shall be increased with increasing extract concentration, but it cannot be higher than the oxygen evolution potential of the solution at a particular pH value. This mentioned oxygen evolution potential can be set as an upper boundary.

According to the Pourbaix diagram of water, the oxygen evolution potential of the solution showing a pH of 2.30 is equal to 1.093 V_{SHE} [41]. This value is 0.852 V for saturated calomel electrodes. Additionally, it is the maximum possible value for pitting potential. No pitting potential can be higher than this value in an acidic solution of pH 2.30. As mentioned in the previous paragraph, the lower boundary of the pitting potential was 0.027 V_{SCE}. The calculation of an improvement in pitting potential can be performed according to these two boundaries. If the extract addition gives exactly the same pitting potential of 0.027 V_{SCE}, it can be considered as a 0% pitting potential improvement (%PPI). Additionally, if the extract addition gives the pitting potential of 0.852 V_{SCE}, which is the upper boundary, it can be considered as a 100% pitting potential improvement (100%PPI).

By applying a linear relationship between the pitting potential ($E_{pit}$) and the pitting potential improvement (%PPI), the pitting potential improvement equation can be formulated between the lower boundary and the upper boundary. The slope for this equation was $(100 - 0)/(0.852 - 0.027)$ or 121.21. The intercept was calculated using one coordinate and the slope which was $100 - (121.21 \times 0.852)$ or $-3.27$. The equation for this work is shown in Equation (4).

$$\text{%PPI} = 121.21(E_{pit}) - 3.27 \quad (4)$$

The calculated pitting potential improvements in percentage (%PPI) according to this equation are listed in Table 2. Besides the $E_{pit}$, the %PPI is an alternative parameter for pitting behavior evaluation. The %PPI indicates how far the pitting potential (from the sample with extract addition) is located from the pitting potential obtained from the sample without extract addition in a percentage. The %PPI of 304 stainless steel in a hydrochloric acid solution was found to be increased with increasing *Terminalia bellirica* fruit extract concentrations. It was increased almost two times (from 16% to 29%) after the extract concentration was increased from 100 to 300 mg L$^{-1}$. No significant improvement was obtained as the extract concentration further increased to 400 mg L$^{-1}$. The %PPI was at 29% and 27% for 300 and 400 mg L$^{-1}$ of extract concentrations, respectively. Nevertheless,
this suggested an increase in the pitting resistance of 304 stainless steel by the extract. In this study, the highest pitting potential improvement of 29% was obtained from 300 mg L\(^{-1}\) of extract concentration.

### 3.4. Scanning Electron Microscopy

To confirm the pitting inhibition of *Terminalia bellirica* fruit extract, two samples of 304 stainless steel were separately immersed in the solution with and without extract addition. The potential for chronoamperometry was set at 0.100 V\(_{\text{SCE}}\), which was higher than the pitting potential of 304 stainless steel without extract addition but lower than the pitting potential of 304 stainless steel with 300 mg L\(^{-1}\) of extract concentration. At this potential, the sample without extract addition was already in the transpassive region (pitting region in this case). However, the sample with extract addition was still in the passive region. At the same potential, the *Terminalia bellirica* fruit extract clearly showed pitting inhibition. No pit was observed at 0.100 V\(_{\text{SCE}}\) on the surface of the 304 stainless steel when the extract was added (Figure 7).

![Figure 7. Scanning electron micrographs of type 304 stainless steel surface (a) without extract addition at 0.100 V\(_{\text{SCE}}\) (b) with extract addition of 300 mg L\(^{-1}\) at 0.100 V\(_{\text{SCE}}\).](image)

### 4. Conclusions

*Terminalia bellirica* fruit extract can decrease the corrosion current density and increase the pitting resistance of 304 stainless steel in a hydrochloric acid solution. A very high corrosion inhibition efficiency (%IE) of 95% is obtained with an extract addition of 300 mg L\(^{-1}\). The physical adsorption of the extract molecule leads to corrosion inhibition. The Langmuir adsorption isotherm model can be used to describe the adsorption of the extract molecule on 304 stainless steel surfaces. Besides the conventional pitting potential (\(E_{\text{pit}}\)), the pitting potential improvement in percentage (%PPI) is calculated and can be used to quantify the pitting behavior of 304 stainless steel. The highest pitting potential improvement of 29% is achieved at 300 mg L\(^{-1}\) of extract addition.

**Author Contributions:** Conceptualization, S.S.; methodology, S.S.; formal analysis, S.S.; investigation and data curation, S.S., C.W., N.S. and N.A.; resources, S.S.; writing—original draft preparation, C.W., N.S. and N.A.; writing—review and editing, S.S.; supervision, S.S.; project administration, S.S.; funding acquisition, S.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by special project program, Department of Chemistry, School of Science, KMITL.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to thank Synchrotron Light Research Institute for the support of the FT-IR microscope. The authors are also thankful to Western Digital (Thailand) Co., Ltd., Ayutthaya, Thailand for the electrochemical equipment in the research laboratory.

**Conflicts of Interest:** The authors declare no conflict of interest.
References


3. Chen, Y.X.; Tong, J.; Ge, L.L.; Ma, B.X.; He, J.S.; Wang, Y.W. Ethyl acetate fraction of *Terminalia bellirica* fruit inhibits rat hepatic stellate cell proliferation and induces apoptosis. *Ind. Crop. Prod.* 2015, 76, 364–373. [CrossRef]


23. Baskar, P.; Rathinapriya, P.; Prabakaran, M. Use of *Trociodendron Araliae* extract as green corrosion inhibitor for mild steel in 1M HCl solutions. *Processes* 2022, 10, 1480. [CrossRef]


**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.