ADSORPTION CORROSION INHIBITIVE BEHAVIOR OF PEELS EXTRACT OF *Theobroma cacao* ON MILD STEEL AS A CORROSION INHIBITOR IN HCl MEDIA

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**ABSTRACT**

*Theobroma cacao* peels extract (TCPE) obtained from the result of the maceration of cacao peels with methanol. TCPE contains an organic compound that can be used as a corrosion inhibitor. This compound has an advantage in being non-toxic and biodegradable. The essential compound of TCPE was analyzed by using Gas Chromatography-Mass Spectra (GC-MS) before fractions. This essential compound was characterized to obtain a high content of oxygen which leads to its capability to control the corrosion. Corrosion properties of mild steel in hydrochloric acid (HCl) solution by the use of TCPE were determined by conducting Electron Impedance Spectroscopy (EIS) method. Surface analysis by Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX), X-ray Photon Spectroscopy (XPS), and X-ray Diffraction (XRD) was also performed to produce corrosion inhibition properties of TCPE in HCl solution. Inhibition efficiency and resistance polarization were figured out to increase with increasing concentration of the essential compound in TCPE. The Nyquist plot showed the charge transfer-resistant increase with increasing the inhibitor concentration. Energy activation and heat absorption from corrosion indicate that TCPE is absorbed on the steel surface. This absorption can occur through chemical impingement of inhibitor atoms or molecules on surfaces of metal. This phase is a spontaneous process and is followed by Langmuir isotherm absorption. Adsorption occurs at the surface in a mild steel surface is evidenced by the results of testing SEM-EDX, XPS, and XRD. It can be concluded that the addition of TCPE is very promising to be used in minimizing the rate of corrosion of mild steel.

**Keywords:** *Theobroma cacao* Peels, Essential Compound, Mild Steel, XPS, XRD

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**INTRODUCTION**

Cacao is one of the commodities that role is quite important to the national economy as a provider of employment, income and foreign exchange in Indonesia. Cacao exports rank third in the plantation sector accounts for foreign exchange, after rubber and palm oil. With a production capacity of 712,231 tons in 2012 and 2015 is estimated to reach 1 million tones. The exports of cacao reached 148,590 tons in 2014 an increase of 26.5% as compared to 2009 with estimated export capacity 250,000 tons in 2015.1 By assuming the same rate, it is estimated to be around USD 160 billion in 2015. Increasing cacao production, however, leads to an increase the number of waste cacao peels. The largest component (around 75%) of cacao fruit is the skin of the fruit or commonly called cacao pod or peel. The cacao peels production in 2009, for instance, reaches 850 thousand tones, and thus leaves the cacao peels waste around 640 thousand tons.1 Since the cacao production increases every year, it is estimated that there is around one million tons of cacao peels garbage in 2020. If such waste is not handled properly, this becomes a serious environmental problem in the near future. While the cacao peels contain polyphenol compounds that can be used as a corrosion inhibitor.2 Meanwhile, on the other side, iron and steel in particular steel are widely used in industry due mainly to its adequate formability, high strength and low cost. However, it is easy to corrode when in contact with
air, acid solution, de-scaling, and in the chemical process.\(^3,4\) Therefore, it is necessary to reduce corrosion rate by using inhibitor from natural extract.\(^4,5,6\) Corrosion inhibitor is a chemical compound that is added to a liquid or gas to reduce the corrosion.\(^5\) Inorganic inhibitors are commonly used up to now such as chromate, phosphate, molybdate and others. These compounds are good anti-corrosion abilities, but most of them are toxic to humans and the environment. It is not also easily decomposed and thus causes pollution to the environment.\(^7,8\) It is, therefore, organic inhibitors become more popular as green corrosion inhibitors. Some plant extracts containing hetero groups such as nitrogen, sulfur and oxygen has been then promoted as new green inhibitors.\(^3,9\) Some fundamental investigation, however, is still necessary to obtain every chemical, physical and mechanical aspects of the applying green inhibitor to protect mild steel in a corrosive medium.

As reported in the previous article\(^2,6\) the addition of a small amount of *Theobroma cacao* peels leads to a decrease in the rate of corrosion and increases the usability of inhibitor the steel by 1.5M hydrochloric acid medium. In order to describe the corrosion mechanism in the detail, and the compound that takes part in controlling the inhibition, the extract and corrosion product will be observed by GC-MS and FTIR. The corrosion behavior is also studied by weight loss and potentiodynamic methods. Some parts of the previous experimental procedure and the results will be appeared again here for remembering and make the connection with the previous article. In the previous article, the discussion emphasis an attempt to slow the rate of corrosion on the steel surface by using inhibitors of the cacao peel extracts, which are agricultural waste, which has not been treated optimally. This article is there because of the interest to find out what is happening in the steel surface after reacting with cacao peels extracts.

**EXPERIMENTAL**

### Preparation Materials

The composition of cacao peels extract and mild steel was obtained by using the GC-MS-QP2010S Shimadzu column and a Foundry-Master Xpert Spectrometry. Nicolet FTIR spectrophotometer is used to analyze functional groups of its compound. Corrosion rate and inhibition efficiency are calculated by the Potentiodynamic Method by using the instrument of potentiostat EDAQ Potentiostat 466-Advanced Electrochemical System. Analysis of the microstructure of mild steel has been obtained by using a microscope Olympus BX51. Analysis of the mild steel surface before and after corrosion was observed using an optical microscope Trinokuler and S-3400N Scanning Electron Microscopy. All of their procedures in this study have been described in a previous article.\(^2,6\)

### Polarization Resistance (Rp)

Corrosion testing using polarization resistance techniques aims to see the resistance of the sample toward oxidation when exposed by the external sources. Polarization resistance is the relevant approach to gauge the rate of corrosion and the usability of inhibition without affecting metals by using Stern-Geary formula the following equation 1:

\[
Rp = \frac{\frac{ba \times bc}{I_{corr} \times 2.303 (ba+bc)}} \times 100\%
\]

Where: \(I_{corr}\) = current density, \(ba\) = anodic Tafel slope and \(bc\) = cathodic Tafel slope

### Electron Impedance Spectroscopy (EIS) Method

Method of EIS is applied to figure out the charge transfer resistance and double-layer electrical interface mild steel with a solution. This method uses the procedures as in the Tafel method. Electrochemical parameters which attained are \(Rs\), \(Rct\) and \(Cdl\), wherein \(Rs\) is the resistance of solution, \(Rct\) is charge transfer resistance while \(Cdl\) is the deal with the electric double layer capacity. The basic operation tool is tested Open Circuit Potential (OCP) to figure out the stability of the surface of the electrode and to examine the solution. Frequency amplitude used during testing of 10 mV peak to peak, range from 0,1Hz to 100Hz. The inhibition efficiency is resolved by equation 2:

\[
%IE = \frac{[Rct_{(inh)} - Rct]}{Rct_{(inh)}} \times 100
\]

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Where: IE is inhibition efficiency, Rct and Rct (inh) are the charge transfer resistance of the metal in solution absence and the presence of inhibitors.

RESULTS AND DISCUSSION

Microstructure Analysis
The previous results research the mild steel composition used in this study are: Fe (97.8), Mn (0.9), P (0.07), C (0.32), Si (0.22), S (0.06), Cr (0.1), Cu (0.3), Mo (0.02) Al (0.006), Co (0.0053), Ni (0.08) by % weight. These results indicate that mild steel is used to include low carbon steel. The data is supported by the results of microstructure testing in Fig.-1. The picture shows that the microstructure of mild steel consists of ferrite is white, and pearlite is black. Number of ferrites greater than pearlite, this indicates the ductile of the mild steel used.6,10

Gas Chromatography-Mass Spectrometry Analysis
The analysis of the GC-MS spectrum of cacao peels extract before fractionation showed at previous article11 has 42 compounds from its spectrum in Table-1. When the compound contains: three benzene groups, one amide, five carboxylic acids, three monoterpenes, one aromatic, five alkanes, three alcohols, two ketones, and one steroid and the others remain unidentified because of the lack of supporting data. This table shows the inhibitory effect of TCPE is attributed to the presence of organic compounds. Theobroma cacao peels extract consist of various organic compounds of aloft molecular weight with heteroatom within the chemical structures.12,13 However, synergetic and antagonistic effects could affect the inhibition efficiency of Theobroma cacao peels extract as an inhibitor since it has a number of compounds.14 Though once phenolic compounds were instrumental in the process of corrosion inhibitors, compounds of phenolic with hetero groups can be utilized to covalent or coordinate bonds on the mild steel surface.2,12,15

| Name of Compound | Formula | Retention Time (min) |
|------------------|---------|----------------------|
| 2-pentanon 4 hidroxi-4 methyl | C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> | 4.450 |
| Alpha pinene | C<sub>16</sub>H<sub>16</sub> | 7.158 |
| Beta-pinene | C<sub>16</sub>H<sub>16</sub> | 8.125 |
| Trans-beta-ocimene | C<sub>16</sub>H<sub>16</sub> | 8.917 |
| Beta-terpinyl acetate | C<sub>13</sub>H<sub>26</sub>O<sub>2</sub> | 9.292 |
| Benzenamine | C<sub>7</sub>H<sub>9</sub>N | 9.619 |
| Eugenol | C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> | 15.108 |
| 2,3,4,4,-tetra prophyl-1-(trimethylsilyl) -1,3 diaza - 2, 4 diborabutane | C<sub>16</sub>H<sub>24</sub>B<sub>2</sub>N<sub>2</sub>OSi<sub>2</sub> | 15.250 |
| Phenol-2 methoxy-(2-propenyl) | C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> | 15.875 |
| Phenol-2 methoxy-(1-propenyl) | C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> | 16.483 |
| Tetra decane | C<sub>14</sub>H<sub>30</sub> | 17.542 |
| Silicate anion tetramer | C<sub>24</sub>H<sub>75</sub>O<sub>12</sub>Si<sub>12</sub> | 17.775 |

Fig.-1: Microstructure of Mild Steel, (a)20x, (b) 50x, and (c)100 x magnification6
Changes in the value of $b_a$ and $b_c$ and Tafel curves presented in the previous article indicate that the adsorption of the cacao peels extract is a modification of the anodic dissolution at the anode and the hydrogen evolution at the cathode. Tafel curve is clear that both the cathode and anode reaction inhibited, and the inhibition process in line with the increase in the concentration of TCPE in acidic solution, but more polar in the cathode. Value detainee’s linear polarization, calculated using the Stern-Geary equation. Increased polarization resistance showed by using the cacao peels extract can inhibit the movement of the electron which occurs at the surface of mild steel or oxidation reaction is able to be inhibited so that the process can be protected as a result of corrosion of steel corrosion rate decreased. Positive relationships among the extract concentration and resistance polarization with the efficiency of inhibition can be seen in the chart (Fig.-2). The figure shows the increase in the concentration extract could withstand the rate of corrosion of mild steel. Increasing the extract concentration will lead to the increase of resistance polarization and the move of electrons from the surface to a solution of mild steel can be inhibited, so it will increase the efficiency of corrosion inhibition efficiency on the surface of mild steel. It means that increasing efficiency also increasing the polarization resistance as can be seen in the chart in Fig.-2.

The properties corrosion of mild steel in 1.5M HCl was also surveyed by using EIS. EIS measurements in HCl medium in the room temperature and atmospheric pressure are mentioned in Nyquist plots. Figure-3 shows that the mild steel plot in the electrolyte solution in absence and presence several extract
concentration of cacao peels at room temperature. Generally, the impedance spectra from the mild steel corrosion in the HCl solution includes whether one depressed capacitive loop (one time-constant in Bode-phase representation) or two capacitive semicircles (two well-defined time-constant in Bode-phase format). The Bode plots of steel in HCl 1.5M absence and presence extract of cacao peels as shown in the charts in Fig.-4 and Fig.-5.

 Mostly, Nyquist plots result do not describe as the half-circle, yet in the form of a semi-circle. It associated with the dispersion frequency because of the roughness and homogeneity in the electrode surface. Following the literature, the inhomogeneous films EIS spectra on the surface of metal or harsh and absorptive electrodes are analyzed using the finite transmission line and the filmed equivalent circuit mode. These methods are usually employed to study the degradation of coated metals. EIS spectra for the metal covered by organic inhibitor films are considered as the failed coating metals. It means, in the current research the filmed equivalent circuit model is applied to figure out the inhibitors-covered metal/solution interface. Moreover, Figure-4 and Figure-5 describe the one time-constant in Bode-phase.

Inhibitors were added to the media, and it increases the value of the impedance electrode solution interface, in particular the value of Rct. It indicates the inhibitors suppresses the transmission of the electrons from the steel surface into the solutions which decrease iron atoms oxidation and reduce the H⁺ ions. Electrochemical parameters on the different concentrations of the inhibitor are shown in Fig.-6 and Table-2. The data from the table shows by the increase of the extract concentration, the Rct values increased as well while the Cdl values decrease. The decrease of Cdl likely deals with the absorption of organic molecule on the mild steel surface which decrease the constant of dielectric and/or increase the electrical double layer thickness. The relationship between inhibition efficiency Rct with clearly visible in Fig.-6, where the increase in Rct was also followed by an increase in the efficiency of inhibitory.
Isotherm of Adsorption

The communication of the surface of the metal and the inhibitor can be studied by adsorption isotherms. The graph plots the log (θ / (1 - θ)) vs. log C and θ vs. log C gives a straight line indicates that the inhibitors are used to meet the Law Langmuir adsorption isotherm. A linear relationship was obtained such as correlation coefficients in Table-3, which ranged between 0.95-0.97 with different time variations. This shows there has been a strong molecular effect among the particles and the surface adsorption of steel, where the interaction was raised by the increase of concentration of inhibitor. Adsorption occurs on the surface of mild steel will increase the surface of surface coverage.

Thermodynamic Parameters

The energy activation (Ea) and enthalpy change (ΔH) from the slope of the curve Arrhenius plot v vs log 1/T and log v/T Vs 1/T are given in the previous journal. Ea changes indicate that the inhibitor
participates in the electrode or may alter the difference of potential of the metal interface with adsorption.\textsuperscript{21}

Table-3: Coefficients of Correlation R Obtained From the Comparison of the Concentration of the Inhibitor with the Surface Coverage

| No | Time (Hours) | Concentration of Extract (%) | R     |
|----|-------------|-----------------------------|-------|
|    |             | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |       |
| 1. | 48          | 0.0 | 0.9982 | 1.5509 | 2.1124 | 2.3485 | 2.5971 | 0.9587  |
| 2. | 96          | 0.0 | 1.0515 | 1.5873 | 2.1991 | 2.4193 | 2.7902 | 0.9726  |
| 3. | 192         | 0.0 | 1.1052 | 1.6316 | 2.3332 | 2.6144 | 2.8293 | 0.9532  |
| 4. | 384         | 0.0 | 1.3011 | 1.8653 | 2.4732 | 3.1746 | 3.0384 | 0.9648  |
| 5. | 768         | 0.0 | 1.4278 | 2.2119 | 2.6321 | 3.3750 | 3.4530 | 0.9531  |

Fig.-5: Bode Plots of log Z vs Frequency for Mild Steel in HCl 1.5M in the Absence and Presence of a Different Concentration of Cacao Peels Extract

Fig.-6: The Relationship between the Efficiency of Inhibition and the Rct of the Cacao Peels Extract Concentration

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A negative value of $\Delta G$ indicates that the adsorption takes place spontaneously process. While the value $\Delta H$ greater than 20 kJ/mol indicates that the mechanism of inhibition and adsorption on the mild steel surface occurs chemically. The amount of adsorption occurs on the surface of mild steel in 1.5M hydrochloric acid at different concentrations of cacao peels extract is based on Langmuir adsorption isotherms. Whereas the entropy change showed the increase by the use of inhibitors cacao peels extract. So that the interaction between mild steel with extracts of cacao peels will increase, consequently the corrosion rate can be inhibited and the efficiency increased.

**Surface Morphology Analysis**

Analysis of the surface of mild steel and the formation of the passive layer by the without and with of inhibitors are obtained by employing optic microscope Trinokuler and a S-3400N Scanning Electron Microscopy with 2000x magnification has been described in the previous article. To remind the figure of it can be shown at Figure-7. To clarify that of the Figure-8d shown that the cacao peels extract could restrain the rate of corrosion by producing a layer on the surface of the steel. This layer protects the surface of mild steel toward corrosive ions and will decrease electrochemical reactions corrosion rate.

![Fig.-7: SEM Images of Mild Steel in HCl 1.5M after 32 Days Dyeing at Room Temperature (a) Before Dyeing (Polished), (b) Dyeing Inhibitor, (c) Dyeing HCl Absence Inhibitor, and (d) Dyeing HCl with Inhibitor 2.5 %](image)

**SEM-EDX Analysis**

The test toward mild steel surface and passive layer formation in HCl 1.5M were done for 32 days both using inhibitor and without inhibitors from cacao peels extract using SEM are described in Fig.-7. The figure shows there a hole formed on the surface of mild steel in HCl by the without of both polar extract of Theobroma cacao peels as well as the absence of the pit corrosion products. However, by the use of cacao peels extract as well as the use of holes on the steel surface, it forms a passive layer on the surface to protect the surface against the corrosions. The layer protects the surface against the corrosive ions and slow down the electrochemical reactions and will eventually reduce the corrosion rate.

The test toward ingredients of C and Fe on the mild steel surface by using HCl 1.5M was done 32 days both using the cacao peels extract and without the extract using SEM-EDX. Figure 8 shows the atomic percentage of element C is increased from 0.3% to 16.90% by the presence of the extract of cacao peels. In can be inferred that the steel surface adsorbed the C atoms of the molecule of the cacao peels and produce a passive layer on the surface. Moreover, the element Fe decreased from 98.79% to 37.43% by the presence of peels extract of cacao. It suggests that the Fe forms a complex compound with polar extract of cacao peels which can decrease the percentage of Fe atoms. Figure-8a shows that the elements did not consist O element, while in Figure 8b shows a low percentage of element O. Moreover, Figure-8c shows the increasing of oxygen percentage to 63.54%. It is because of the medium of corrosive which is dyeing in HCl 1.5M without inhibitor. Then, the oxide is rapidly formed along with the corrosive ions from hydrochloric acid. However, by the use of the extract of cacao peels inhibitors, the corrosive ions are eliminated because of the passive layer in the form of organometallic complexes on the surface of mild
Hence, it decreases the corrosion rate and oxides formed as becomes 44.89% O levels as indicates in Figure 8d. The elements and oxides checked in the SEM-EDX analysis are mentioned in Fig.-9.

![Figure 8](image-url)

**Fig.-8:** Curve the Surface of SEM-EDX, a. Mild Steel, b. Mild Steel with Extracts, c. Mild Steel in HCl 1.5M, and d. Mild Steel in HCl with 2.5% Extract

**XPS Analysis**

XPS analyses aim to know the film that is formed due to adsorption on the surface of soft steel as in Fig.-10. Its figure shows the results of XPS analysis of the film in several variations of the sample surface. Spectra that appear in Fig.-10a show that the layer on the surface of the film contains constituent of C, O, and Fe. Figure-10b detected the bond of carbon (C, C-C, C=C) that appears at the peak of 284.5 ev. Carbon-oxygen single bonds (-CO) on 285,7ev also a carbon-oxygen double bond (-C=O) on 288.4ev, as well as a combination of single and double bonds (OC=O) in 289,3ev. This data is supported by FTIR analysis with the advent of spectra at 1019 cm⁻¹, 1162 cm⁻¹, 1435-1459 cm⁻¹ and 1617-1654 cm⁻¹ wavelength. The combination is assumed to be a complex compound cacao peels extract with oxygen in the form of TCPE₂O₃, TCPE (OH)₃ and TCPE-OC products.

However, spectra O1s appear to represent a signal of the 529,8ev oxide and oxygen of the hydroxyl group at 531,4ev and 533,0ev as in Fig.-10c. Hydroxyl groups appear suitable by FTIR analysis results of (3376-3422) cm⁻¹ wavelength. Figure-10d shows the peak that arise consists of a mixture of iron corrosion products such as Fe₃O₄, Fe₂O₃, FeO, FeCO₃ and FeOOH. The peak began to appear at 710 and 724 ev. The results analysis of oxides of XPS reinforced by FTIR for the oxide of steel at a wavelength of 668 cm⁻¹.
**Fig.-9:** The Summary of Oxides and Constituent were analyzed by the SEM-EDX with Variation Treatment

![Graph](image)

Where: ST-O : Steel Only  
ST-HCl-EP : Steel + HCl + Polar Extract  
ST-HCl : Steel + HCl  

**Fig.-10:** XPS Spectra of: (a). TCPE were analyzed, (b). Oxygen is inhibited and not inhibited, (c). Carbon is adsorbed, and (d) Fe appears on the surface of the steel

**XRD Analysis**

Analysis of XRD results in Fig.-11 was conducted on three variables: mild steel, mild steel which is immersed in HCl absence and presence the addition of the peels extracts of cacao. Three spectras of the sample in Figure 11 shows only the peak of the iron spectra showed no significant difference. These results indicate that the layer film is formed on the surface of the iron oxide. From the resulting compounds, it is seen that 3 of these compounds is a common product of corrosion on steel that is: the form of FeO, Fe₂O₃ and Fe₃O₄. The products of corrosion can cause damage to the morphology of the surface of the steel in the form of focused corrosion or corrosion evenly. The alleged
emergence of a compound FeO, Fe₂O₃ and Fe₃O₄ based content 3 most dominant elements are Fe, O, and C is supported also by the results of testing and discussion XPS, SEM, and EDX earlier.

Fig.-11: XRD Spectra of the Samples with the appearance of Oxide at each peak (a) Mild steel, (b) Mild steel immersed in hydrochloric acid, and (c) Mild steel immersed in hydrochloric acid in the with peels extract of cacao

**CONCLUSION**

The results of GC-MS showed that there are many secondary metabolites in the peels extracts of cacao. Functional groups of the compound were confirmed by FTIR, heteroatom-containing group inhibit the corrosion by performing coordinate covalent bond on the mild steel surface. The extract of Cacao peels can be adsorbed on the surface of mild steel by forming a passive layer. The use of cacao peels extracts inhibitors prevents the movement of electrons from the surface into the solution which indicates from impedance measurements. It decreases the iron atoms and H⁺ ions during the process of oxidation. XPS and XRD indicate the compounds in cacao peels extract forms a corrosion inhibitive layer by contacting with irons on the mild steel surface. It is concluded that there is a strong correlation between efficiency inhibitions of cacao peels extract inhibitors with adsorption isotherm in steel surfaces, so that corrosion rate can be inhibited.

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