Chapter 10

Theobroma cacao Peel Extract as the Eco-Friendly Corrosion Inhibitor for Mild Steel

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Additional information is available at the end of the chapter

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Abstract

Corrosion control for metals has technical, economical, environmental, and aesthetical importance. The use of corrosion inhibitors from natural product is one of the best ways to slow the rate of corrosion of metals and alloys. The use of extract inhibitors from natural product is the best alternative because it does not contain heavy metals and is nontoxic, environmentally friendly, biodegradable, easy to obtain, inexpensive, and available in large quantities. The organic compounds contained in the extracts of natural products such as tannins, amino acids, phenolics, and alkaloids contain heteroatomic groups, which can inhibit corrosion rate and are interesting to study. With the development of science and technology, many methods are used to protect the corrosion, such as electroplating and coating, and organic inhibitor shows real promise such as *Theobroma cacao* peel extract. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. The addition of polar extract of cacao peel into a solution of HCl 1.5 M is very effective to reduce the attack surface corrosion on mild steel and can maintain its mechanical properties. This chapter consciously restricts itself mainly to plant materials, especially *Theobroma cacao* peel extract, as green corrosion inhibitors.

Keywords: *Theobroma cacao,* corrosion inhibitor, plant product, coating

1. Introduction

Nowadays, steels are applied in a variety of needs, like constructions, buildings, bridges, cars, industry tools and installation such as water treatment, oil and waste. The steel is chosen as it is accessible and easily fabricated with high tensile strength. Nevertheless, the most weaknesses of this steel are easily undergone corrosion in corrosive medium [1], like in acid environmental condition during the acid cleaning process, acid solution transportation, storage, de-scaling, and pickling process. The frequently used acid solution in pickling process by industry is hydrochloride acid [2].

Corrosion problem is a major and serious one as it is related with the working safety, economics, environmental damage, and health. Generally, industry takes the above-average steel, which is made from mild steel. The lost caused by this corrosion in Indonesia is huge, reaching 1.5 billion rupiah per year. Some estimate that this loss is up to 2–3.5% of the GNP. This cost included the maintenance expense, the replacement for the material, working hours, and the lost benefits due to the stop of production, customer dissatisfaction, administration fee, physical lost, and health treatment [3].

In order to reduce the loss because of the corrosion on the steel, the protection for the steel should be done. Many attempts have been made to slow the corrosion rate such as coating, material selection, changing the environmental condition, design selection, painting, anodic and cathodic protection, and inhibitor substance addition into corrosive medium [4]. A frequently used way in preventing the corrosion is taking a particular inhibitor. This corrosion inhibitor derives from organic and inorganic substances which consist of groups of free electron or substances with heteroatom group of P, N, S, O like nitrate, chromate, phosphate, urea, phenylalanine, imidazoline, and amine compounds for inorganic one. The functional group within this compound can be adsorbed on the steel surface, and then, it is bonded to one another, forming the film layers, which can inhibit corrosion reaction. In fact, synthetic material that is used as inhibitors is dangerous to living organisms, relatively high in price, and environmentally harmful [5]. Organic compound like polyphenol derives from natural extract or natural products. They are an easy-to-use natural material which can be used as an alternate inhibitor as it is safe, readily available, biodegradable, low cost, and eco-friendly [2, 6].

Recently, there have been many researches that focus on finding a new source for corrosion inhibitor particularly on plants. Parts of the plants that can be taken for the research are leaves, barks, fruits, heartwoods, or roots. Several extracts of natural product that have been studied as eco-friendly corrosion inhibitors can be seen in **Table 1**.

On another side, Indonesia is well known as the largest cacao producer in the world, certainly resulting in the largest solid waste as well. The production of this waste reaches 60–70% of the total fruit production or six times of the dried cacao peels production [24]. In 2013, cacao production was 800,000 ton with 600,000 ton waste. By having the National Cacao Movement in the area of 1.6 million acres, it is estimated that in 2014, the production increases into 1.1 million ton. The raise in production is in the synergy with the raise of dried cacao peels into 825,000 ton [25]. As the government program becomes priority to recycle the waste into useful products, the use of this cacao peel waste becomes the corrosion inhibitor, which is one of the alternatives to reduce the pollution. Cacao peel extract contains several chemical compounds such as flavonoid or condensed tannin like antosianin, tannin, catechin, and leucoanthocyanidin. Tannin is a complex organic compound which consists of polyphenol and has a number of hydroxy groups where sometimes it occurs in the form of glycosides. Tannin is known as tannic acid or galatanat acid. As the inhibitor, it can replace the use of lead oxide or chromate, which is frequently added into paint for protecting steel corrosion [23]. Not many has paid attention on the use of cacao peel extract which acts as the inhibitor on mild steel, and it is documented, whereas its waste is readily available in great number. Thus, in order to balance

No.	Metal	Inhibitor source	Media corrosive	Inhibition efficiency (%)	Reference
1	Mild steel	*Lawsonia inermis*	HCl	92.06	[2]
2	Steel	*Azadirachta indica* leaves	HCl	60.40	[7]
3	Mild steel	*Palicourea guianensis*	HCl	89.00	[8]
4	Mild steel	*Murraya koenigii leaves*	HCl, H_2SO_4	94.50	[9]
5	Steel	*Phyllanthus amarus*	H_2SO_4	98.00	[10]
6	Carbon steel	*Pachycormus* leaves	HCl	93.50	[11]
7	Mild steel	*Emblica officinalis* leaves	HCl	88.60	[12]
8	Mild steel	*Euphorbia hirta* leaves	H_2SO_4	90.90	[13]
9	Mild steel	*Ananas comosus* L	HCl	91.02	[14]
11	Steel	*Prosopis cineraria*	HCl	86.67	[15]
12	Mild steel	*Uncaria gambir*	HCl	86.45	[16]
13	Mild steel	*Acacia Senegal*	HCl	90.32	[17]
14	Mild steel	*Argan hulls*	HCl	97.30	[18]
15	Mild steel	*Centella asiatica*	HCl	95.08	[19]
16	Mild steel	*Laurus nobilis*	H_2SO_4	87.60	[20]
17	Mild steel	*Musa acuminate*	HCl	96.00	[21]
18	Mild steel	*Dodonaea viscose*	HCl	95.40	[22]
19	Mild steel	*Theobroma cacao peels*	HCl	96.26	[23]

Table 1. Green inhibitors used for corrosion inhibition of metal.

and preserve the nature, the use of this waste should be applied more in order to be useful, like to be the eco-friendly inhibitor.

The object of this study is mild steel. It can be found on public needs for example railings, concrete bailout, and others; however, it easily undergoes corrosion. The corrosive medium used in this study is hydrochloric acid, and cacao peel extract acts as the inhibitor which slows down the corrosion rate.

Inhibition efficiency on cacao peel extract in chloride acid medium is set by applying the weight loss method, whereas its inhibition mechanism was learned based on Gibbs adsorption free energy analysis (ΔG_{ads}), the value of activation energy (Ea), SEM, EDX, FT-IR corrosion product spectrum analysis, and electrochemical parameters which derive from potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS). However, for its inhibition effect on mechanical property, the hardness and tensile tests are applied.

2. Corrosion inhibitor

Corrosion inhibitor is the solution which is added in inconsiderable quantity to slow down or to prevent the reaction between the steel with its medium. The inhibitor has a role to form the barrier from one or several molecular layers on the acid attack, salt, and other corrosive environment [26]. Sulfur and nitrogen containing heterocyclic with their varied substituent are effective as the corrosion inhibitor. Inorganic compounds such as phosphate, chromate, dichromate, silicate, borate, molybdate, and arsenate compound have been found effective as the steel corrosion inhibitor. Pyrrole and its derivatives are shown as the best protection to corrosion in acidic medium. The major weakness of this inorganic inhibitor is its toxicity, inorganic products, difficulty to degrade, and containing heavy metal. The safest alternative in reducing the corrosion rate is by using inorganic compound which consists of polar function group like nitrogen, sulfur, and oxygen, where they can be used as an effective inhibitor [27]. This corrosion inhibitor works effectively to prevent the corrosion rate in various ways, and the inhibitor adsorption on the steel surface is one of the mechanisms for anodic corrosion inhibitor. The adsorption that occurred is physisorption and chemisorption or chemisorption, which is proceeded by physisorption. However, the adsorption occurred is up to the inhibitor structure itself, the type of the steel, and the media condition (pH, temperature, and inhibitor's number) [28].

The plant extract contains heteroatom organic compound that can slow down the corrosion rate; meanwhile, O, N, S, and P are the active center of adsorption process on steel layer [27, 29, 30]. The presence of free pair of electron in inhibitor molecule causes the electron transfer from inhibitor toward the steel surface as the coordination of covalent bond is formed. The characteristics of this compound inhibition are derived from the molecular adsorption ability, and polar group acts as the reaction center on adsorption process. The resulted layers of adsorption separate the steel from the corrosion media [31, 32].

Nevertheless, the nutrition in the cacao peels is considered high enough, and the waste of cacao production also contains alkaloid theobromine compounds (3,7 dimethyl xanthine), flavonoid or condensed tannin such as antosianin, tannin, katekin, and leucoanthocyanidin [33–38]. Tannin, which is present in cacao peels, contains active group functioned as corrosion inhibitor [36].

Tannin compound is able to form complex with steel(II) and steel(III). Steel(II) complex tannin is colorless, dissolved, and oxidized easily. In the presence of oxygen, it turns this complex into steel(III) complex tannin which is called tannat. The newly formed compound is well known as organometallic surface complex. It is the one that clings onto the steel surface and prevents the further corrosion process as this complex is absorbed onto the steel surface and protects it [33].

3. Research method

The equipment for this study is as follows: measuring cups, analytical balance, digital caliper, grindstone, oven, Heidolph WB 2000 *rotary evaporator*, *hot plate*, cutting machine, sand paper with the roughness of 80, 120, 400, 600, 1000, 1500 mesh, 3 mm drilling machine, electron microscope, *Foundry-Master Xpert Spectrometer*, GCMS-QP2010S SHIMADZU, LC–MS-QMicro QAA 842, P*otensiostat* eDAQ, Potentiostat/Galvanostate AUTOLAB PGSTAT 320 N *Electrochemical Impedance Spectroscopy (EIS), Perkin Elmer System 2000 Fourier Transform Infrared Spectroscopy (FTIR), Hitachi S3400 N Scanning Electron Microscopy (SEM)* and *SEM–EDX* by using *EMAX software, Universal Testing Machine type RAT-30P CAP,* and *Rockwell Hardness Tester TH 550*.

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4. Results and discussion

4.1. Analysis of chemical composition and microstructure of mild steel

The chemical composition of used mild steel in this study is 0.32% C, 97.8% Fe, 0.22% Si, 0.10% Cr, 0.20% Mo, 0.90% Mn, 0.06% S, 0.30% Cu, and 0.07% P. It is referred to AISI 1035 (ASM) steel standard and supported by microstructure of mild steel testing as seen in **Figure 1**. This microstructure consists of the white color ferrite and the black color pearlite with a ratio of 1:2. This condition shows that the mild steel used in this study contains lesser Fe_3C than pure Fe; therefore, it is resilient [39].

4.2. Analysis of methanol extract of cacao peels

The testing result of phytochemical shows that cacao peel extract contains secondary metabolite compound such as alkaloid, terpenoid, phenolic, flavonoid, and steroid. Further identification is analyzed by using GC–MS. GC–MS spectra result before fractionation indicates that cacao peel extract contains of 42 dominant compounds (spectra peak). To identify the inhabitance of polar compound in cacao peel extract that acts as inhibitor, further analysis using LC–MS is carried out. The LC–MS identification results 10 dominant peaks as seen in **Figure 2** and **Table 2**. **Table 2** displays the compounds which are identified by LC–MS containing compounds with higher molecular weight referred to fragmented ion and molecule ion from the testing data [40]. These compounds have heteroatom group which functions as the corrosion inhibitor as well [26].

4.3. Analysis of Fourier transform infrared

FTIR analysis is carried out on cacao peels, free extract corrosion product, and corrosion product with cacao peel extract in HCl 1.5 M solution. Several peaks on those three spectra undergo friction; however, amount of peaks are occurred on almost similar frequency or adjacent. Identified functional group from cacao peel extract is phenolic, aromatic ring, and

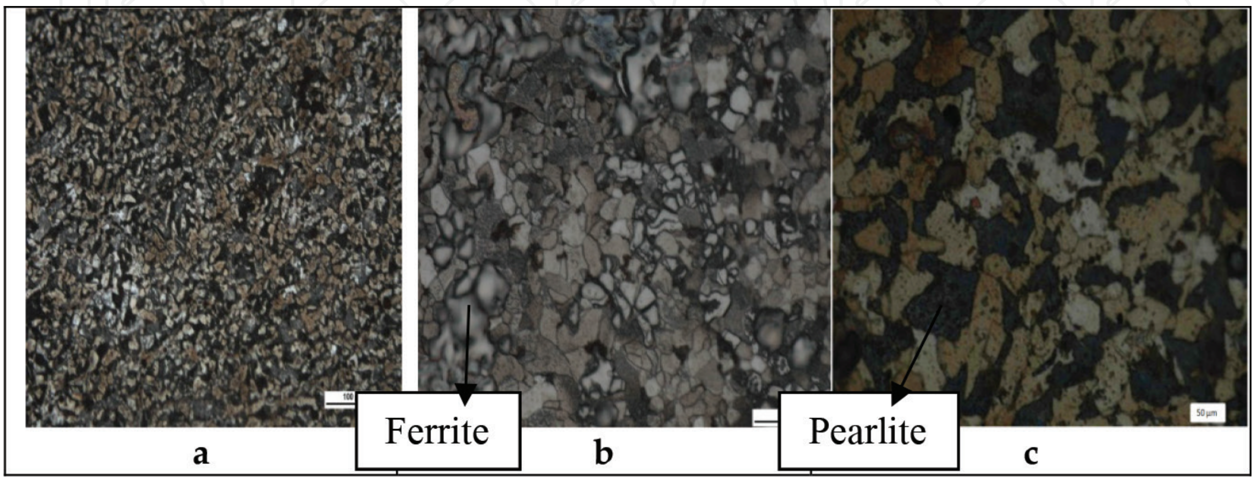

Figure 1. Microstructure of mild steel sample displayed: (a) 20×, (b) 50×, and (c) 100× magnification.

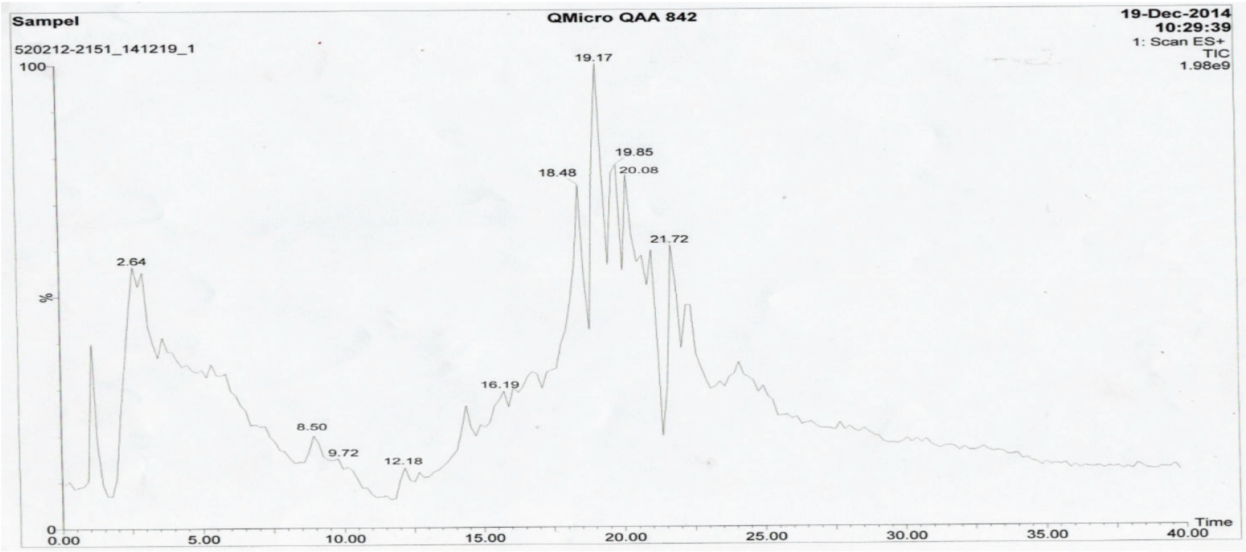

Figure 2. The chromatogram of cacao peel extract by using LC–MS.

Compound name	Formula	Retention time (min)
Quercetin	$C_{15}H_{10}O_7$	2.64
Catechin	$C_{15}H_{14}O_6$	8.50
Gallic acid	$C_7H_6O_5$	9.72
Epicatechin	$C_{15}H_{14}O_7$	12.18
Catechin	$C_{15}H_{14}O_6$	16.19
Caffeic acid derivate	$C_8H_{10}N_4O$	18.48
Salvianolic acid	$C_9H_{10}O_3$	19.17
Kaempferol 3-O-rutinoside	$C_{15}H_{10}O_6$	19.85
Procyanidin B_2	$C_{31}H_{28}O_{12}$	20.8
Kaempferol 3-O-(sinapoyl)-sophoside	$C_{53}H_{56}O_{28}$	21.72

Table 2. Analysis of cacao peel extract compound which has been fragmented by LC–MS.

ether [41]. Some of these functional groups are appeared in corrosion product but with a slight shift of frequency friction. The occurrence of friction and the disappearance of several peaks on particular frequency indicate that there is interaction between cacao peel extract and mild steel in HCl 1.5 M solution. The result shows the interaction and chemical bound between extract compound and metal on the surface area [4]. Identified functional groups from peaks are shown in **Table 3**.

4.4. Analysis of mild steel corrosion rate

The measuring result of corrosion rate and inhibition efficiency by using the weight loss method shows that adding extract cacao peels into corrosion medium causes the corrosion rate becoming

FTIR spectrum peak, ν (cm^{-1})			Functional group identification
Cacao peel extract	Corrosion product		
	In HCl 1.5 M without extract	In HCl 1.5 M with 2.5% cacao peel extract	
—	668	—	Fe—O
1051	1020	1019	C—O (str)
1400	—	—	C—C=C (aromatic)
—	1458	—	C—C (aromatic)
1603	1636	1629	C=O (str)
—	2359–2342	2363	C—H (str)
3422	3385	3376	O—H (phenolic)

Table 3. FTIR spectra analysis of cacao peel extract, corrosion product, and its identification.

lesser and conversely an increase in inhibition efficiency as seen in **Figure 3**. It was due to the larger iron surface coated with molecules on the cacao peel extract. Cacao peel extract molecules that coat the metal surface are adsorbed into the steel surface and form passive layer that protects the steel from active ion's corrosion attack in the acid solution. Formed passive layers are derived from oxygen and functional group, which is in cacao peel extract [42–44].

Natural product extract is compounds containing atom with free electron pair and can be used to covalent coordination bond [7]. This atom is electron donor that can form complex compounds with iron existed in the mild steel. It is a stabile complex compound, not easily oxidized, and coats the mild steel surface so that the corrosion can be restrained [19].

Figure 3 means that the increase of extract concentration decreases the corrosion rate and on the other hand increases its inhibition efficiency. However, the increasing time during submersion makes the corrosion rate increase as well, and decreases its inhibition efficiency on

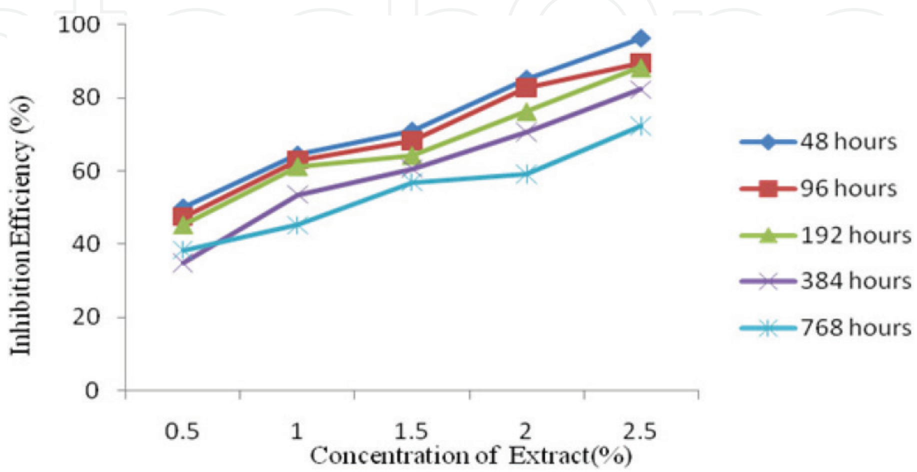

Figure 3. The effect of extract concentration on steel corrosion inhibition efficiency in HCl 1.5 M with different submersion time.

similar concentrate. It is due to the increasing time during the submersion that causes more weight loss and triggers desorption [45], so that the smallest corrosion rate and the biggest efficiency are obtained for 2-day (48-h) submersion duration by adding 2.5% extract.

In order to see the interaction in mild steel in the absence and the presence of cacao peel extract within HCl 1.5 M, temperature variation is applied starting from 303 K to 323 K. In **Figure 4**, it can be seen that the rate corrosion decreases where the inhibition efficiency increases by the rise of added cacao peel extract concentration. However, the corrosion rate is increasing, and inhibition efficiency is decreasing by the rising temperature. The increase of corrosion rate and the decrease of efficiency by the increasing temperature are caused by the increase of adsorption strength on high temperature or inhibitor molecule desorption occurred [46].

Constantly, inhibitor molecule adsorption and desorption have taken place on the steel surface until the balance of the two processes reached the certain temperature. The highest efficiency value is 83.91% for 2.5% extract concentration on 303 K temperature [47].

4.5. Potentiodynamic polarization method

Mild steel polarization curve on varied extract concentration in HCl 1.5 M has been extrapolated into Tafel plot as shown in **Figure 5**. Corrosion current value (I_{corr}), corrosion potential (E_{corr}),

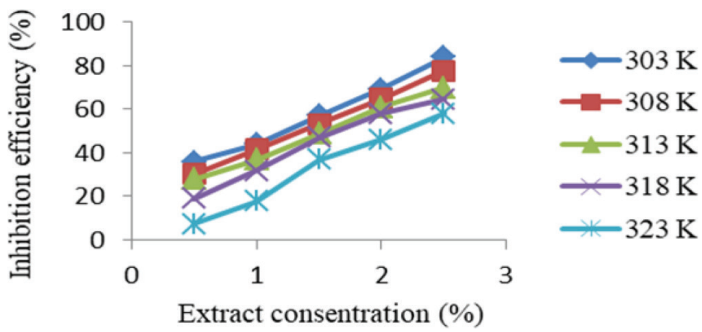

Figure 4. Extract concentration effect on mild steel corrosion inhibition efficiency in HCl 1.5 M of temperature variation.

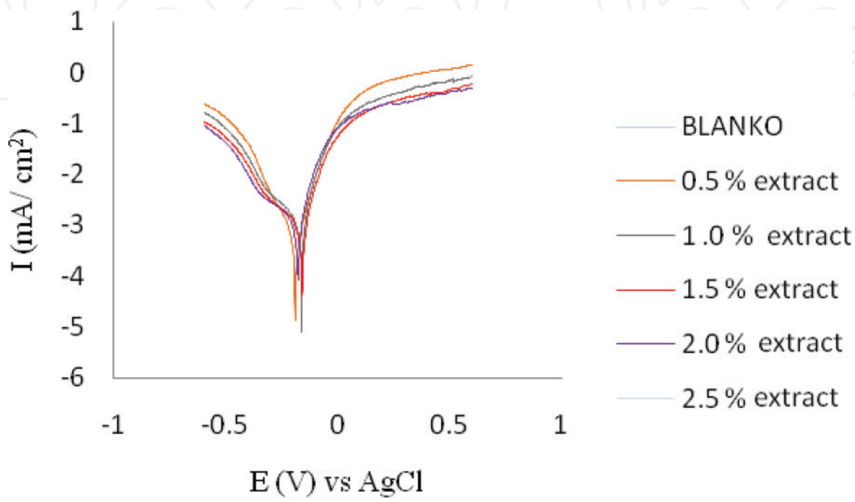

Figure 5. Potential Tafel plot steel polarization in HCl 1.5 M with variation of cacao peel extract concentration.

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cathodic and anodic constant (b_a and b_c), and inhibition efficiency on each treatment obtained from Tafel line extrapolarization are shown in **Table 4** [48]. Measuring the corrosion rate by using Tafel plot began with determining the corrosion current value and corrosion potential.

Table 4 shows that the increasing extract concentration in the medium will decrease the I_{corr} value. The highest I_{corr} value is seen on the immersed sample in the medium without 2.5% additional extract, whereas the lowest I_{corr} value belongs to the sample with 2.5% additional extract. Comparing inhibition efficiency testing result weight loss and potentiodynamic polarization results relatively similar value.

The table shows the E_{corr} friction value where the lowest E_{corr} value belongs to medium without additional extract which is −0.28 V, and the highest with additional extract medium which is −0.20 V. This corrosion potential value friction toward more positive and negative ways indicates that the additional extract is anodic and cathodic [49, 50]. Undoubtedly, it demonstrates that cacao peel extract influences the anodic dissolution on mild steels and at the same time slows down hydrogen evolution reaction on cathode [2, 51]. This result is clearly shown that this extract is a mixed-type inhibitor [48, 52].

4.6. Analysis of polarization resistance

The change in value of b_a and b_c displayed in **Table 4** indicates that cacao peel extract adsorption is modification of anodic dissolution and hydrogen evolution on cathodic. In **Figure 5**, it is obviously seen that these two cathodic and anodic reactions are inhibited, and to some extent, its inhibition process is in line with the increase of cacao peel extract concentration in acidic medium; conversely, cathodic is more polarized [53–55]. The polarization value linear resistance is measured using Stern-Geary Eq. (1) which its result can be seen in **Table 4**.

$$\mathrm{Rp} = \frac{b_a \times b_c}{I_{corr} \times 2.303(b_a + b_c)} \quad (1)$$

b_a and b_c are anodic and cathodic constants.

The resistance polarization (Rp) measuring result undergoes an increase with the rise of extract concentration. This increasing polarization resistance shows that the use of cacao peel

Cons. inhibitor (%v/v)	I_{corr} (mA cm^{-2})	E_{corr} (Vdec^{-1})	b_a (Vdec^{-1})	b_c (Vdec^{-1})	R_p (m^2)	IE (I_{corr})	IE (R_p)
Blank	0.06	−0.28	2.4	1.71	6.87	—	—
0.5	0.016	−0.27	2.8	2.3	34.48	74.81	80.07
1.0	0.013	−0.25	3.67	2.57	52.05	80.03	86.6
1.5	0.0078	−0.2	2.00	1.60	57.36	87.48	88.02
2.0	0.007	−0.22	5.25	2.63	115.26	89.54	94.04
2.5	0.005	−0.28	5.71	2.67	157.99	92.08	95.64

Table 4. Parameter of mild steel corrosion in HCl 1.5 M in the absence and the presence of cacao peel extract obtained from polarization measurement.

extract slows down electron transfer on steel surface or is capable to inhibit its oxidation reaction, so that corrosion process can be protected. It makes the steel corrosion rate decrease [53].

Positive relation between polarization resistance with extract concentration and polarization resistance with inhibition efficiency is shown in **Figure 6**. This figure points out the increasing of extract concentration can slow down mild steel corrosion rate. Due to the fact that the additional extract concentration, increases the polarization resistance, the transfer electron from mild steel surface to solution can be inhibited, and it makes the corrosion inhibition efficiency on the mild steel surface increase as well [55].

4.7. Electrochemical impedance spectroscopy

The result of EIS measurement for mild steel corrosion in HCl 1.5 M is recorded by Nyquist diagram as seen in **Figure 7**. This behavior can be related to frequency dispersion of electrode surface roughness [55]. The difference on Nyquist diagram between blanks and the presence of inhibitor is clearly seen. In the medium with additional inhibitor, there is impedance value increase on electrode interface solution, particularly Rct value [56]. The EIS measuring result in **Figure 7** shows that the additional inhibitor impedes the electron transfer from the steel surface into the solution.

The increase of Rct value results in the decrease of iron atoms' oxidation process and ions' H^+ reduction process [8]. Electrochemical parameter on the inhibitor concentration variation can be seen in **Table 5**. This table clearly shows connection between Rct with inhibition efficiency and capacitance (Cdl). The increase of Rct is also followed by the increase of inhibition efficiency value [4] and in similar with the decrease of capacitance with the increase of extract concentration [48]. The capacitance value is obtained by using the following formula (2):

$$\mathrm{Cdl} = \frac{1}{2\pi f_{max}\,\mathrm{Rct}} \tag{2}$$

where Cdl = double layer capacitance, f_{max} = maximum imaginer frequency from obtained impedance, and Rct = charge transfer resistance.

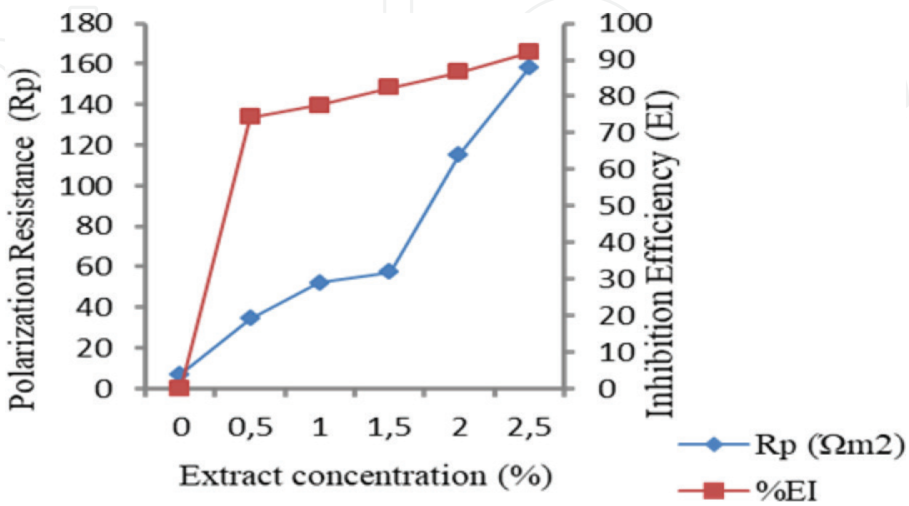

Figure 6. The effect of cacao peel extract concentration on polarization resistance and mild steel inhibition efficiency in HCl 1.5 M.

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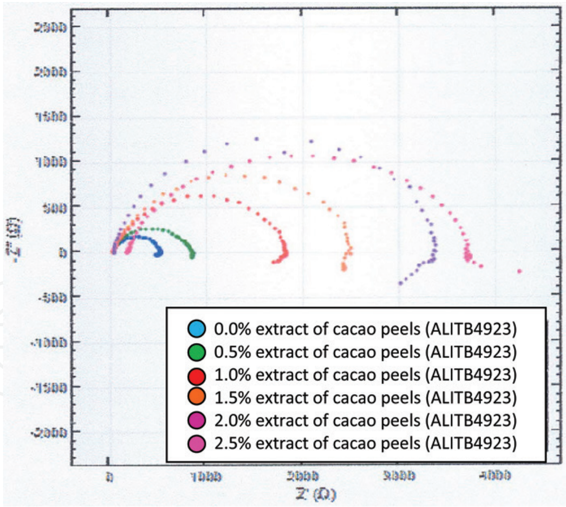

Figure 7. Nyquist plot steel in HCl 1.5 M solution with variation of cacao peel extract concentration.

Inhibitor concentration (%)	Rs (Ω)	Rct (Ωcm²)	Cdl (μFcm²)	EI (%)
0.0	34.0	505	0.63	0.0
0.5	23.0	850	0.31	40.9
1.0	23.3	1680	0.16	69.94
1.5	22.2	2435	0.093	79.26
2.0	32.4	3259	0.081	84.50
2.5	181	3552	0.075	85.78

Table 5. Relationship of extract concentration with electrochemical parameter in HCl 1.5 M medium.

The decrease of Cdl value in **Table 5** can be connected to the decrease of local dielectrical constant or the increase of layers thickness on mild steel surface due to the presence of adsorption on this surface [57, 58]. Besides that, the decrease of capacitance value might occur due to the hydro-molecule changes which adsorbed on the steel surface with cacao peel extract molecules [58]. It can be also the formation from the film layers with the interaction between inhibitor molecules and atom Fe on the mild surface which involves the chemical and physical reactions. Thus, inhibitor molecules are coating more to the active side and press the corrosion reaction with the increase of extract concentration. It causes that the charge transfer between the steel surface and solution is going to be tough and corrosion reaction is inhibited more effectively [59].

The inhibition efficiency of the cacao peel extract produced depends on the inhibitor concentration and corrosive medium used. In the graph, it can be seen that the inhibition efficiency in HCl solution can reach 96.26% (weight loss), 95.64% (IE), and 92.08 (I_{corr}) with 2.5% concentration of inhibitor as shown in **Table 4**. This happens, because the Fe-tannin complex is formed on the surface, covering the entire surface of the steel. Comparison of three methods for testing the efficiency of inhibition of polar extract of cacao peels on mild steel is shown in **Figure 8**.

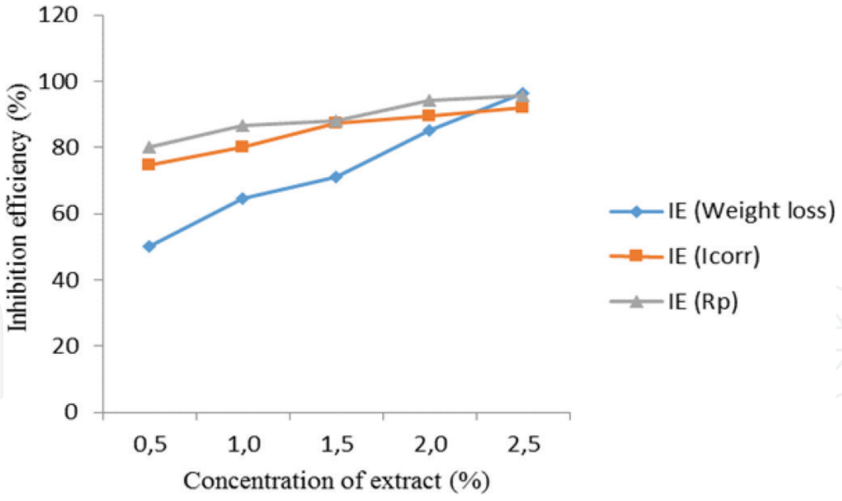

Figure 8. Inhibition efficiency against concentration of extract in HCl 1.5 M.

4.8. Analysis of adsorption isotherm

Cacao peel extract adsorption on mild steel is characterized by using degree data of surface coating from the weight loss data obtaining through experiment with the formula (3) as follow:

$$\theta = \frac{V_0 - V_1}{V_0} \quad (3)$$

In order to obtain clear and accurate data to find out the adsorption on the mild steel surface, adsorption isotherm of Langmuir, Temkin, and Frumkin adsorption is applied. Interaction phenomena between metal surface and inhibitor can be studied from the adsorption isotherm. Those three adsorption isotherms show linear relationship between extract concentration with the adsorption occurred on the mild steel surface. This linear relationship is proven by the correlation coefficient value in **Table 6** in the range of 0.90–0.97, with different time variation.

Nevertheless, the strongest relationship from one out of those three adsorption isotherms is Langmuir with the correlation coefficient reaching up to 0.97. These data indicate that the inhibitor which is used here fulfills the Langmuir adsorption isotherm rule [8, 44]. **Figure 9** shows that the more the immersion time with the increase of extract concentration, the more

Time (h)	Correlation coefficient (R^2)		
	Langmuir	Temkin	Frumkin
48	0.9587	0.9415	0.6081
96	0.9726	0.9595	0.5573
192	0.9532	0.9327	0.3340
384	0.9648	0.9447	0.3454
768	0.9531	0.9082	0.9171

Table 6. Correlation coefficient (R) obtained from various isotherm adsorption on varied immersion time.

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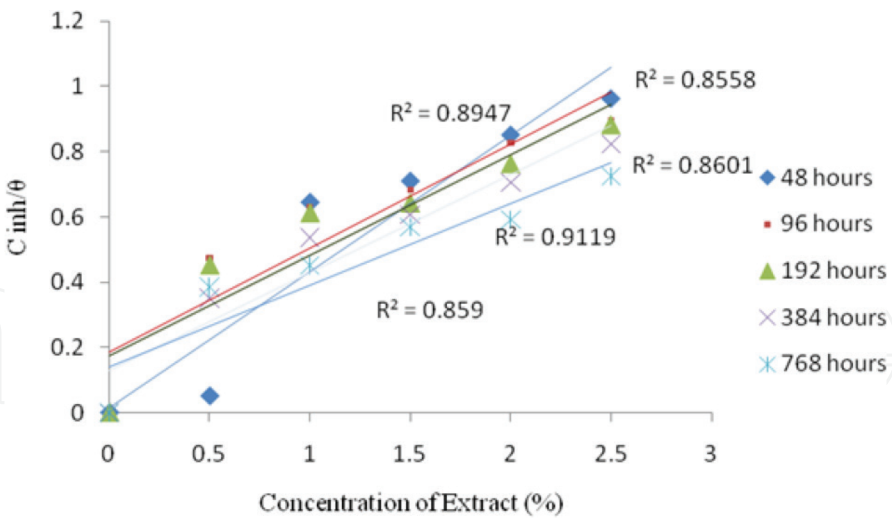

Figure 9. Langmuir adsorption isotherm of cacao peel extract on mild steel surface in HCl 1.5 M with different temperature.

the adsorption occurred on the mild steel surface. It demonstrates that the strong molecule interaction has occurred between adsorption particles and mild steel surface, where the interaction increases with the raise of added inhibitor concentration [60].

4.9. Analysis of thermodynamics

The thermodynamic data are obtained from experiment on temperature effect and adsorption isotherm. These data can complete the basic information on the interaction between cacao peel extract and steel surface. The temperature effect on steel corrosion rate is studied through HCl 1.5 M in the absence and presence of cacao peel extract at the temperature of 303–323 K. The resulted straight line represents good correlation between corrosion rate and temperature, where the increase of the temperature is followed by the increase of corrosion rate; however, there is a decrease in its inhibition efficiency. This sign explains that the film layer is formed during physical adsorption [58].

The increase on entropy value by the addition of cacao peel extract shows that the regularity degree is lower. The friction of entropy value to positive way indicates that complex is formed on certain level, and causes the regularity degree becoming higher. This formed complex will impede the corrosion rate on metal surface [52]. The thermodynamic data in **Table 7** are strengthening the conclusion made that cacao peel extract can act as the corrosion inhibitor. The regularity degree or entropy change (ΔS) is obtained by applying the following formula (4):

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

4.10. Analysis of surface morphology

Analysis of mild steel surface and the forming of passive layer on its surface in HCl 1.5 M in the absence and the presence of cacao peel inhibitor is studied by using SEM scaled up 2000× as seen in **Figure 10**.

Indicator	Ea (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol)
Blank	142.3782	217.6073	—	0.32
Blank + inhibitor	198.8048	196.1433	−19.89	0.58

Table 7. Kinetic and thermodynamic parameters of mild steel with and without cacao peel extract in HCl 1.5 M.

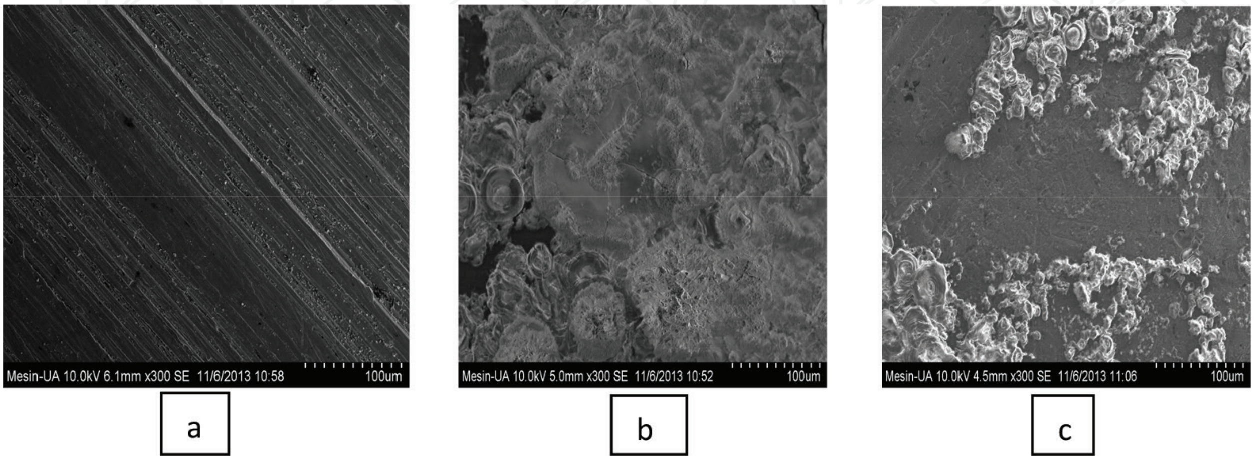

Figure 10. SEM photograph of mild steel (a) before being immersed and has been polished, (b) immersed for 32 days in room temperature by HCl 1.5M in the absence of inhibitor and (c) immersed for 32 days in room temperature by HCl 1.5M in the presence of 2.5% inhibitor.

Figure 10a shows the surface morphology from steel sample where fine lines in white color can be seen and it is relatively thin due to the effect of grindstoning and sanding on the mild steel surface. It is also seen that the surface is still flat, clean, and impermeable and yet has holes. **Figure 10b** is where corrosion product formed and the holes obviously seen and marks that there has been damage occurred on the surface. However, **Figure 10c**, in the presence of cacao peel extract, points out that it minimizes corrosion product and holes on the steel surface by forming passive layers on the surface. This layer becomes barrier on the corrosive ion attack on mild steel surface so that the electrochemical reaction is slowing down, and eventually the corrosion rate is decreasing as well [43, 56].

Analysis of C and Fe elements on mild steel surface in HCl 1.5 M which have been immersed for 32 days in the absence and presence of cacao peel extract is studied by applying SE-EDX. The element recapitulation is represented in **Table 8**. Referred to this table, the percentage of C element decreases by the presence of cacao peel extract, from 0.3% becoming 16.90%. This percentage of C element points out that this atom C of cacao peel extract molecules is adsorbed on the steel surface forming passive layers on the mild steel surface. Meanwhile, the percentage of atom on Fe element decreases by the presence of cacao peel polar extract, from 98.79% becoming 37.43%.

The data presented explain that Fe forms complex compound with cacao peel polar extract, so the percentage of detected Fe atom becomes smaller. Whereas, the Oxygen (O) element which in the beginning has not been detected yet, then by the adding of cacao peel extract can be

Treatment	Element content (% weight)		
	C	Fe	O
The absence of treatment	0.32	98.79	—
Immersion in 2.5% extract	6.19	92.66	4.33
Immersion in HCl 1.5 M	1.50	29.39	63.54
Immersion in HCl 1.5 M with 2.5% extract	16.90	37.43	44.89

Table 8. Identified element contents of the EDX testing on mild steel surface in HCl 1.5 M.

detected with low percentage. Then, there is an increase in percentage of oxygen up to 63.54% due to being immersed in corrosive medium HCl 1.5 M, quickly formed the oxide by the attack of corrosive ions of HCl. Nevertheless, by the help of polar inhibitor cacao peel extract, this corrosive ion attack can be blocked by forming passive layers in the form of metal organocomplex on the mild steel surface, because of the decrease of corrosion rate and lesser oxide been formed which is represented by O percentage becoming 44.89% [2, 50, 54].

4.11. Analysis of mechanical properties

The testing result of hardness and tensile on mild steel is represented in **Figure 11**. This hardness and tensile states an increase by the raise of added extract concentration. It is supported by the testing data of hardness, which shows that the increase of extract concentration adds the hardness on mild steel surface. Therefore, it causes the raise of the steel resistance and decreases corrosion rate due to the higher amount of extract adsorbed on its surface.

These data exhibit that the higher the extract concentration, the wider the mild steel surface which is coated by cacao peel extract. This extract is chemically adsorbed onto the mild steel surface and forms thin film layer that is difficult to be damaged [22]. The amount of extract adsorbed onto the surface is clearly determined by the SEM–EDX testing result as seen in **Table 7**. On contrary, the increase of surface hardness decreases corrosion rate and increases efficiency, and this connection is shown in **Figure 3** [61]. The increase of carbon level on mild steel surface does not only raise the hardness but also improve surface coating degree [62, 63]. The relationship of these four mechanical properties is expressed in **Figure 11**.

4.12. Corrosion inhibition mechanisms

Inhibitor molecules on mild steel surface occurred because of the presence of adsorption. This adsorption is due to the adhesion force between inhibitor and mild steel surface. Inhibitor molecule adsorption on mild steel surface produces thin film layer which can impede corrosion rate. In this case, polar extract inhibitor of cacao peels formed thin layer on the surface which can function as the control of the corrosion rate by making separator between the steel and corrosion media [64]. The process of cacao peel extract adsorption on mild steel surface will occur on functional group [22], where the mechanism can be seen in **Figure 12**.

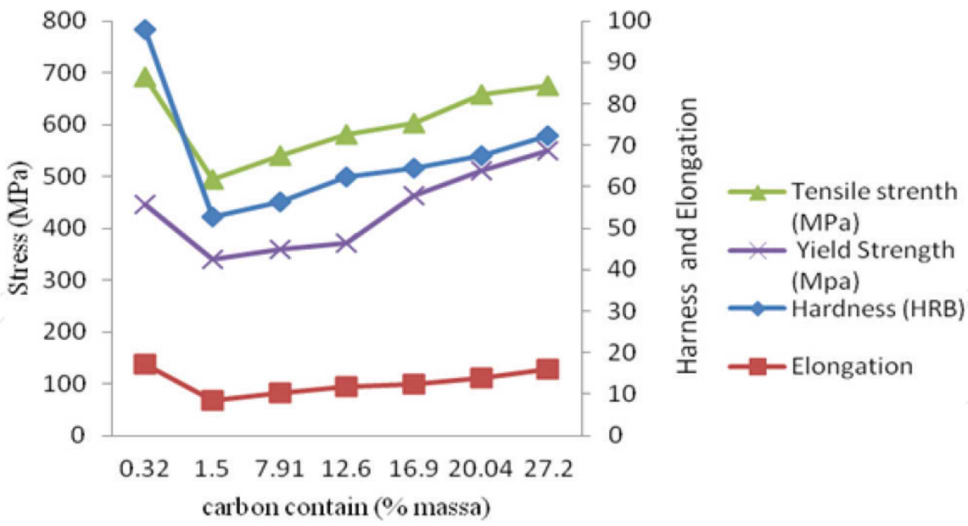

Figure 11. Yield strength, tensile strength, hardness, and elongation against % carbon in surface.

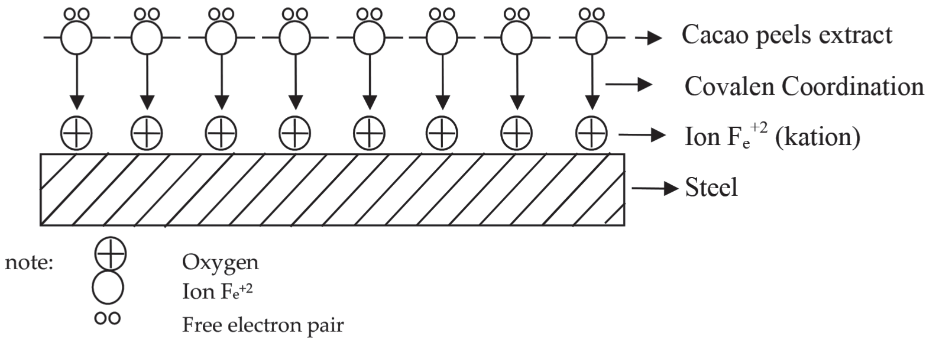

Figure 12. Adsorption mechanism of cacao peel extract on mild steel surface.

The adsorption result expresses that the higher the added inhibitor concentration, the more the metal part which is coated by corrosion inhibitor molecules. The bond occurred during the inhibitor adsorption process on the mild steel surface indicates as coordination covalent bond which involves chemical adsorption. It can be seen that from the struggle to omit the layer and in coherence with perceived enthalpy change value (ΔH) is higher than that with the absence of inhibitor [65].

The mechanism occurred on mild steel surface can be expressed on the basis of adsorption process and constituent structure that is present in the extract. The inhibit process might appear due to the presence of phytochemical constituent adsorption through oxygen atom and/or nitrogen atom on metal surface [22]. Possibly, this complex is absorbed into steel surface through Van der Waals force to form the protection layer in order to prevent the steel from corrosion [66]. Several major constituents of its extract are catechin, kaempferol, gallic acid, procyanidin, and tannin, which are shown in **Figure 13**. Inhibitor effective performance depends on phytochemical constituent measurement of cacao peel extract where its area is wider than the metal surface; so it can minimize the corrosion [2, 22].

Adding cacao peel extract into the solution is highly effective in order to reduce the chloride acid attack on mild steel surface, as compared to other plant extracts as can be seen in **Table 1**.

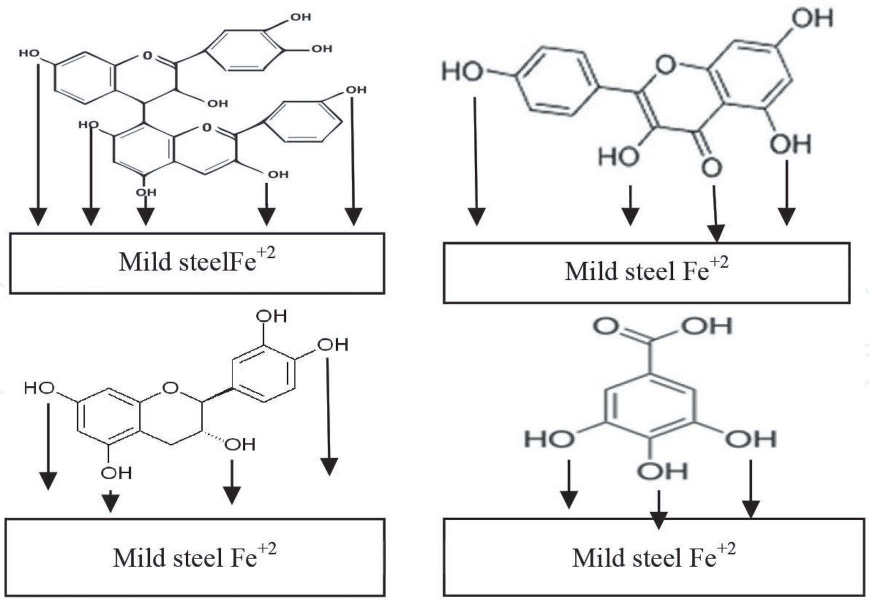

Figure 13. Compound adsorption process existed in cacao peel extract on mild steel surface.

This can be seen from its ability to inhibit on the surface of mild steel greater than other inhibitors at concentrations that are not too different and the same media corrosive hydrochloric acid.

5. Conclusions

By and large, of all researches conducted, it can be concluded that:

1. Cacao peel extract can function as appropriate corrosion inhibitor for mild steel in HCl 1.5 M.
2. GC–MS and LC–MS testing results shows that cacao peel extract contains of many active compounds. These functional group compounds have been confirmed by FTIR test containing heteroatom group which takes a part in corrosion inhibition through coordination covalent bond on mild steel surface.
3. Significantly mild steel corrosion rate decreases by the addition of cacao peel extract. On the contrary, inhibition efficiency increases by the increase of extract concentration up to 2.5%. Even though the efficiency decreases with the raise of work temperature, it is considered high enough reaching the temperature of 323 K. Adding cacao peel extract into the solution is highly effective in order to reduce the chloride acid attack on mild steel surface.
4. Through potentiodynamic measurement and impedance measurements that adding the inhibitor indicate inhibits electron transfer from mild steel surface into solution, so that both oxidation process of iron atoms and reduction process of H^+ ion decrease. Has been determined that the inhibitor extract of cacao peel in HCl are mixed-type with dominant as cathodic inhibitor.
5. Inhibition mechanism between extract and mild steel surface is studied through the interaction between isolated electron pair functioning as donor ion and mild steel surface functioning as acceptor, so that coordination covalent bind formed.

6. Cacao peel extract is chemically adsorbed into mild steel surface by forming Fe organometallic layer on the surface referring to Langmuir isotherm adsorption rules. The adsorption occurred on this mild steel surface influences mechanical properties of hardness and tensile, so it can restore the mechanical properties which has been attacked by corrosion.

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