

Corrosion Behavior of Environmental Friendly Inhibitor of *Theobroma cacao* Peels Extract for Mild Steel in NaCl 1.5 M

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Abstract

In this investigation, the inhibition effect of TCPE (*Theobroma cacao* peels extract) on mild steel in NaCl 1.5 M solution has been studied by using weight loss, potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) methods. Infrared spectra and GC-MS performed to determine the extract compounds that played a role in the inhibition process. Sample surface morphology was observed by using a scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM- EDX). The obtained changes in polarization and impedance parameters values (I_{corr} , R_{ct} and C_{dl}) that has been obtained indicate that the adsorbed protective film grew with the sign of increasing concentration of inhibitor. The adsorption of used compound on mild steel found to obey Langmuir isotherm. Some thermodynamic parameters such as Gibbs energy (ΔG), enthalpy (ΔH), entropy (ΔS) and activation energy (E_a) were calculated to elaborate the mechanism of corrosion inhibition. Based on the results of surveying activity, it revealed that the corrosion rate decreased with the increase of the extract concentration and increased with increasing temperature. Corrosion inhibition efficiency of 91.93 (weight loss) and 85.90% (Tafel), 90.19% (Rp) and 75.23% (EIS) were at a concentration of 2.5% extract. The Schiff base used for investigation was considered an effective inhibitor in reducing the attack surface corrosion on mild steel. in NaCl 1.5 M solution. The obtained results from various techniques were in good agreement.

Keywords: *Theobroma cacao* peels extract; corrosion inhibitor; Tafel; adsorption; GC-MS

1. Introduction

Corrosion is a spontaneous process that occurs in metal to reform previously, as a result of material degradation. An example of materials which can easily be identified as corroded material is mild steel. Mild steel has a high popularity because this type of metals has the ability to be used in a wide variety of needs, easily welded, and relatively inexpensive. Because of this ability then steel is widely used as a commercial commodity to make the construction, automotive industry, machinery industry, automobile industry and the other (Sastri, 2011; Okafor *et al.*, 2012). Because steel is easily corroded it needs maintenance to reduce the corrosion rate. There are several ways to slow the rate of corrosion, namely: the coating, anodic or cathodic protection and with the addition of inhibitor (Sastri, 2011; Gunavathy and Murugavel, 2012). The use of corrosion inhibitors corrosion treatment is one of the most efficient and economical, because the compound will protect the surface of mild steel from corrosive media by forming a passive layer or protective. The use of the usual inorganic inhibitors is less effective and it has a negative impact because it is

toxic and unfriendly environment. Therefore it may be advisable to use of organic inhibitors from natural, non-toxic and biodegradable products (Al-Sehaibani, 2000; Raja and Sethuraman, 2009).

Corrosion inhibitor is a compound that when it is added in small amounts can reduce the rate of corrosion in aggressive media efficiently (Eddy *et al.*, 2010; Loto *et al.*, 2011; Loto, 2012). Commonly used corrosion inhibitor compounds are compounds containing atoms N, P, O, S, or As (Rani and Basu, 2012). Extract has many natural ingredients that attempts to obtain an environmentally friendly corrosion inhibitors, especially derived from extracts of bark, fruit peel (Gunavathy and Murugavel, 2012), leaves (Raja and Sethuraman, 2009; Eddy *et al.*, 2010), and seeds such as *Cacao* (Samuel, 2007). The other research such as *azadirachta indica* (Okafor *et al.*, 2010), rosemary flower (Hasan and Endrah, 2011), *citrus aurantiifolia* (Saratha *et al.*, 2009), carica papaya (Okafor *et al.*, 2010), *Camellia sinensis* (Loto, 2011), *piper nigrum* (Matheswaran and Ramasamy, 2012), *artemisia annua* (Bouyanzer and Hammouti, 2004), catechin (Hussin and Kassim, 2011), *garcinia mangostana* fruit (Vinod *et al.*, 2010), and fenugreek leaves (Noor, 2007).

Cacao peel that is commonly known as a result of plantation waste is potentially used as inhibitors. Until now, it has not been used optimally even it is still largely known as a waste of cacao plantations. The peel is only collected on a closed hole, then, it is disposed around the cocoa plant, or it is used as a mixture fodder. In order to utilize the waste cacao peels, it is necessary to find an alternative utilization which is more efficient and has a higher economic value, for instance it is used as a corrosion inhibitor because the peels of cacao containing metabolites secondary sizable. Among phenolics, flavonoids, terpenoids, steroids and alkaloids, the peel contains more lone electro pairs (Azizah *et al.*, 1999; Osman *et al.*, 2004; Okuda and Ito, 2011). In order to accommodate this need, the writer feels interested to conduct a study to determine the inhibitory power of cacao peels extract to the reaction rate of corrosion of steel in sodium chloride solution.

2. Materials and Methods

2.1. Mild steel sample preparation

The sample used for this study is a low carbon steel (mild steel). Chemical composition testing of mild steel applied a Foundry-Master Xpert Spectrometry. The obtained composition of mild steel can be seen in Table 1. Sample preparation is done by forming a circular piece of mild steel with a diameter of 25 mm and a thickness of 2-3 mm as shown in Fig. 1. After that, the specimen is polished by using SiC emery paper to the size of fineness 120, 600, 800, 1000, and 1500 μm and finally, it is polished with alumina compound. Then its smooth surface is washed with detergent and distilled water, finally, alcohol is used in order to free samples of fat. Then the sample was dried with a hot dryer at a temperature of 30°C for 10 minutes. Ready-made samples is then stored in desiccators.

2.2. Preparation of cacao peels extract

Cacao peel was cleaned from dirt, dust and other materials, and then the peel was chopped into small pieces and dried in the open air without sunlight for 14 days until it was dry. The dry peel was then ground up into powder. Cacao peel powder was measured for 200 grams, put in macerator, and then added 70% methanol in 1 L. Then the mixture was stirred and left in a macerator for 4-5 day. Maceration results were then filtered by using filter paper, and then the filtrate was put in a vacuum rotary evaporator with a Heidolph WB 2000 at temperature of 54-55 °C for 1 hour until a concentrated extract. The extract of cacao peels was used as inhibitors.

2.3. Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infra Red Spectroscopy (FTIR)

GC-MS is used to identify what compound that plays a role in the inhibition of corrosion of mild steel. The composition of the extracts has been studied earlier by using gas chromatography mass spectrometry (GC-MS). Tests were carried out by GC-MS-QP2010S Shimadzu, with parameters of initial column: AGILENTJ%W DB-1, length: 30 m, ID: 0.25 mm, carrier gas: Helium, EI 70 Ev, injection mode: Split, injection temperature: 310°C, column temperature: 70°C and maximum of 324°C for 50 minutes, column flow: 0.5 ml/min, linear velocity: 25.9cm/sec. Then, FTIR test was applied. This test was done to see the functional groups contained in the cacao peels extract. FTIR spectra were recorded in a Nicolet iS10-FTIR spectrophotometer, which extended from 4000 to 400 cm^{-1} , using the KBr disk technique. The samples were characterized by FTIR and analyzed the spectrum produced by the compound functional group table.

Table 1. Chemical composition of mild steel

Mild steel	Chemical composition (% mass)								
	C	Fe	Si	Cr	Mo	Mn	S	Cu	P
Contain	0, 32	97, 8	0, 22	0, 1	0, 2	0, 9	0, 06	0, 3	0, 07

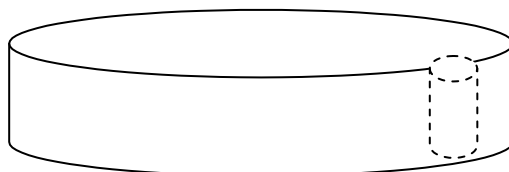


Figure 1. Shape of sample to weight loss test

2.4. Weight Loss Method

Mild steel which has been prepared was measured to determine the initial, then immersed in NaCl 1.5 M corrosive medium for 48 hours, 96 hours, 192 hours, 384 hours and 768 hours, the inhibitor concentration variation was 0.5%, 1.0%, 1.5%, 2.0% and 2.5%. After the corrosion process run for a predetermined time, corrosion products removed from the media corrosion, brushed using a soft brush, then washed with distilled water and finally rinsed with acetone. Then it was dried at room temperature, and then weighed as the final weight. Corrosion rate and inhibition efficiency were calculated with equations 1 and 2 (Okafor *et al.*, 2012; Gunavathy and Murugavel, 2012) the following:

$$V = \frac{\Delta W}{A \times t} \quad (1)$$

$$IE(\%) = \frac{V_{\text{without inhibitor}} - V_{\text{with inhibitor}}}{V_{\text{without inhibitor}}} \times 100\% \quad (2)$$

Where, w is weight loss in mg, A is area of the specimen in cm², t is exposure time in hours, V is corrosion rate and IE is inhibition efficiency

2.5. Electrochemical measurement

First prepared in solution and computer controlled potentiostat instrument EDAQ 466 Potentiostat at Advanced Electrochemical System. Samples to be corrosion, put on holder footage, and dipped in a corrosion cell containing a solution of corrosive media as much as 10 ml. Then put mild steel as the working electrode, auxiliary electrode and electrode comparator into the corrosion cell. Then the three electrodes were connected to the potentiostat instrument. Measured with a scanning speed of 0.1 mV/sec. Measurements will be obtained from the corrosion current density (I_{corr}), corrosion potential (E_{corr}), resistance polarization (R_p). Tafel curves could be obtained while the inhibition efficiency was obtained using the formula 3 (Loto *et al.*, 2011; Noor, 2007) following:

$$IE(\%) = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100\% \quad (3)$$

Where, I_{corr} and I_{corr (inh)} are the corrosion current densities without and with the presence of inhibitors.

Corrosion testing applied the technique of Resistance Polarization; it intended to look at the sample resistance to oxidation when given external potential. Resistance polarization is a good method to determine the corrosion rate and inhibition efficiency without damaging the metal by using the formula 4 (Shyamala and Kasthuri, 2012) following:

$$R_p = \frac{b_a \times b_c}{I_{\text{corr}} \times 2.303 (b_a + b_c)} \times 100\% \quad (4)$$

Where: b_a = Tafel slope of the anodic and b_c = cathodic Tafel slope

2.6. Electrochemical Impedance Spectroscopy (EIS) methods

EIS method used to determine the resistant transfer of electric charge and double layer interface with a solution of mild steel. The procedure with this method is almost the same as the Tafel method. Electrochemical parameter obtained from this test is R_s, R_{ct} and C_{dl}, where R_s is the resistance of the solution, the R_{ct} is the charge transfer resistant and C_{dl} is the capacitance of the electric double layer. Initial operation of the tool is tested OCP (open circuit potential) to determine the stability of the electrode surface and the test solution. At the time of the EIS measurements, this used amplitude of 10 mV peak to peak with a frequency range of 0.1 Hz to 100Hz. The percentage inhibition efficiency is determined by the following equation 5 (Vinod *et al.*, 2010; Eddy *et al.*, 2010):

$$IE(\%) = \frac{R_{ct(\text{inh})} - R_{ct}}{R_{ct(\text{inh})}} \times 100\% \quad (5)$$

Where, R_{ct} and R_{ct (inh)} are the charge transfer resistance of mild steel in solutions without and with the presence of inhibitors.

2.7. Surface analysis

After the corrosion test, surface samples were analyzed by using optical microscopy brand S-3400N Scanning Electron Microscopy. This observation aims to look at the sample surface before and after the occurrence of corrosion.

3. Results and Discussion

3.1. Analysis of GC-MS (Gas Chromatography-Mass Spectrometry)

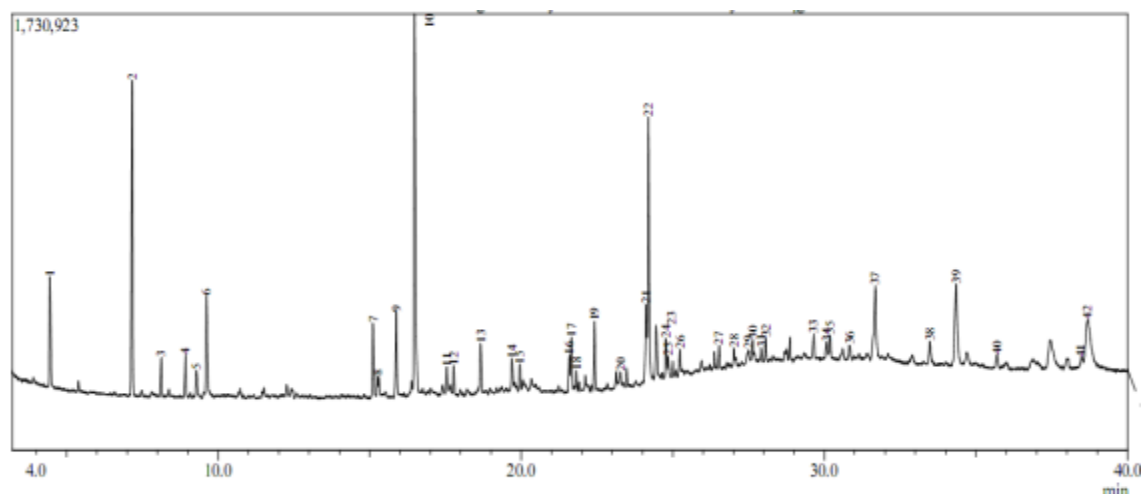


Figure 2. Chromatogram of analysis cacao peels extract by GC-MS

The results of GC-MS spectra showed that the extract of cacao peels contains 42 compounds (spectra peaks) dominant, as can be seen in Fig. 2. These 42 compounds when grouped consists of: 3 benzene groups, 1 amide, 5 carboxylic acid, 3 monoterpenes, 1 aromatic, 5 alkanes, 3 alcohols, 2 ketones and 1 steroid and the rest could not be determined because there is no supporting data. The 8 dominant peaks that promote corrosion inhibition process is presented in Table 2. Peak of phenolic compounds does not appear in the spectrum. Although the initial test phenolic compounds give a blue color with concentrated FeCl_3 , but the results of GC-MS actually show no phenolic peaks.

The absence of phenolic peak compounds indicate that the phenolic compounds in cacao peels extract contains organic compounds with high molecular weight, so that the temperature in the injector is not able to evaporate the phenolic compounds to get to the column (Ferreira *et al.*, 1994). Though phenolic compounds play a role in the process to protect the corrosion, because phenolic compounds having hetero atom groups. It can be used to form a coordinate covalent bond on mild steel surface to protect from

corrosion attack (Sastri, 2011). But the possibility of a non-polar compounds were identified by GC-MS can also provide synergistic and antagonistic effects on the steel corrosion inhibition efficiency (Hii *et al.*, 2009).

3.2. Effect of concentration on corrosion rate

The results of the corrosion test of weight loss method reveal that the addition of inhibitors minimizes weight loss and it will slow the corrosion rate of the initial corrosion rate before being given inhibitor as shown in Figs. 3 and 4. In contrast, the increasing concentration of inhibitor will improve the efficiency of inhibition on the surface of mild steel. It can be seen in Fig. 5. This is because the larger the surface of mild steel in contact with the solution, the more surface coated mild steel by cacao peels extract as presented in Table 3 and Fig. 6. The occurrence of these terms, in accordance with the protection mechanisms that the natural extracts are compounds containing atoms with lone electron pairs (Sastri, 2011; Rani and Basu, 2012). These atoms act as electron donors that will produce complexes with iron (Hussin and Kassim, 2011). These

Table 2. Compounds secondary metabolites contained in the cacao peels extract

Number of Peak	Name of compound	Formula	Retention time (min)
1.	2 pentanon 4 hidroxi-4 methyl	$\text{C}_6\text{H}_{12}\text{O}_2$	4.450
6.	Benzeenamine	$\text{C}_7\text{H}_9\text{N}$	9.619
9.	Phenol-2 methoxy-4(2-propenyl)	$\text{C}_{12}\text{H}_{14}\text{O}_3$	15.875
10.	Phenol-2 methoxy-4(1-propenyl)	$\text{C}_{10}\text{H}_{12}\text{O}_3$	16.483
15.	Benzoic acid	$\text{C}_{16}\text{H}_{33}\text{O}_4\text{Si}_3$	19.950
19.	Hexadecanoic acid	$\text{C}_{17}\text{H}_{34}\text{O}_2$	22.417
22.	Octadecanoic acid	$\text{C}_{19}\text{H}_{36}\text{O}_2$	24.200
42.	Ergastone 3,12-diol (3 alpha, 5 beta, 12 alpha)	$\text{C}_{28}\text{H}_{50}\text{O}_2$	38.675

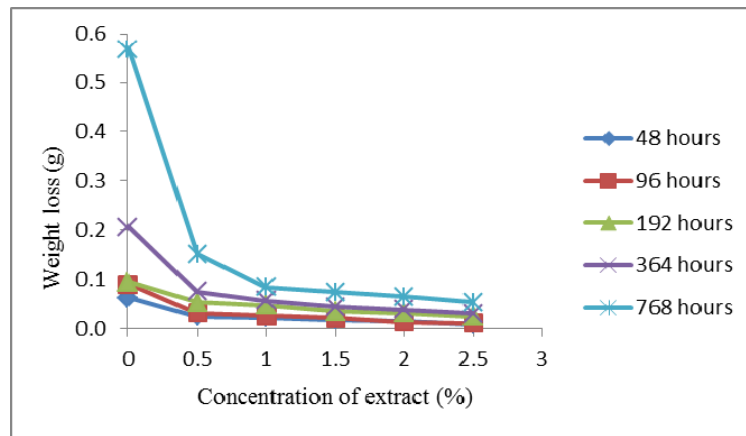


Figure 3. Weight loss against concentration of extract at different time interval

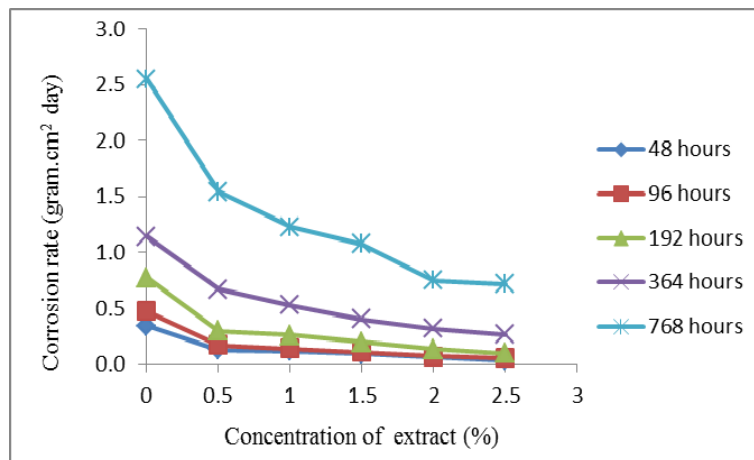


Figure 4. Corrosion rate against concentration of extract at different time

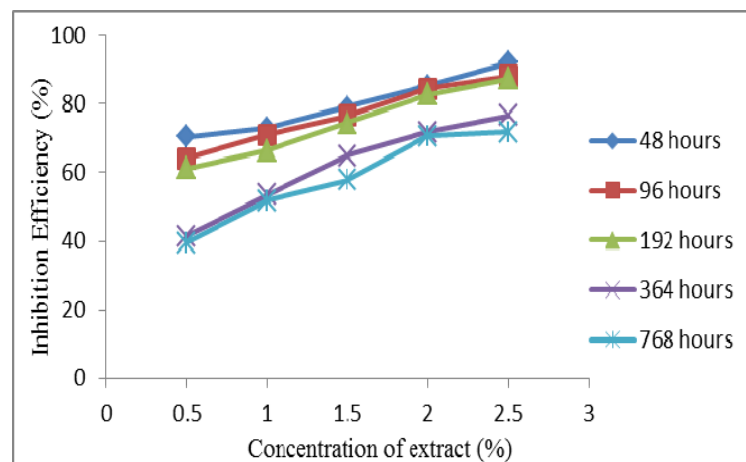


Figure 5. Inhibition efficiency against concentration of extract at different time

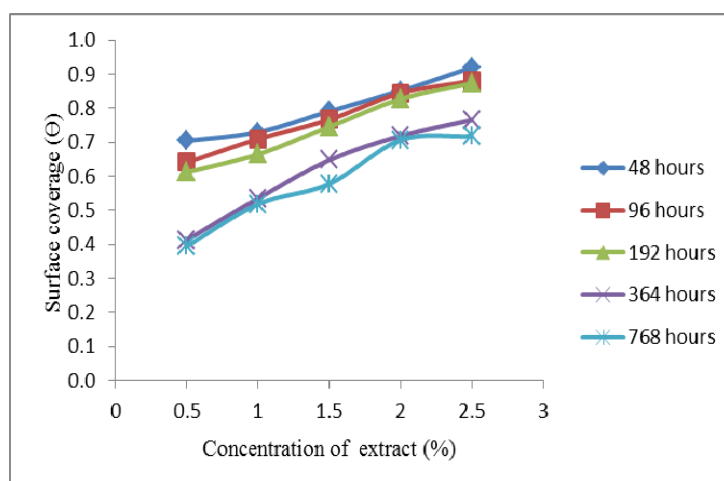


Figure 6. Surface coverage against concentration of extract

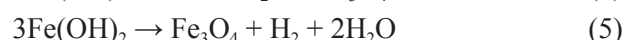
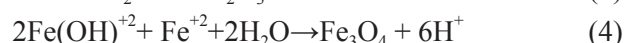
complexes are stable; it will not easily oxidize and will envelop the iron metal surface, so that the rate of corrosion can be inhibited. Therefore, the increase of the inhibitor concentration will also increase the surface coverage (Fig. 6).

3.3. Potentiodynamic polarization method

Calculation of corrosion rate with Tafel curve begins by finding the value of I_{corr} (corrosion current density) and E_{corr} (potential corrosion). I_{corr} and E_{corr} of each sample were obtained from Tafel extrapolation curves. Value corrosion rate of specimens has been tested by potentiodynamic polarization method which was determined by the value of I_{corr} obtained. In Table 3 it can be seen that increasing concentrations of inhibitors in the media will further reduce the value of I_{corr} . The highest value of I_{corr} can be achieved at specimens which were immersed in the media without the addition of inhibitors. On the other hand, the lowest value of I_{corr} was gained by the specimen with the addition of inhibitors of 2.5%. If the test results are compared with weight loss potentiodynamic polarization, it produces the same relative response. It means a decline in the rate of corrosion of the material with increasing concentrations of inhibitors were added (Bouyanzer and Hammouti, 2004; Hussin and Kassim, 2011). Fig. 7 shows an indication of the increasing concentration of inhibitor was added to the media will increasingly shift the curve upward. The shift of curves to more positive value indicates that the inhibitor is added anodic (This means that the cacao peels have a significant effect in inhibiting the anodic dissolution of mild steel in the simultaneously inhibit the hydrogen evolution reaction at the cathode (Shyamala and Kasthuri, 2012; Azzeeri *et al.*, 1982). Lowest E_{corr} value owned by the media without the addition of inhibitors is -0.2800

V, and was highest in the medium with the addition of inhibitors is -0.2000 V. The increase of E_{corr} value will lead to more cathodic seen specimens of the reference electrode. This shows the corrosion potential difference between the two values will be much smaller. When the metal is inserted into the solution, interfacial electrochemical reaction will occur between the metal and the solution. This reaction produces an electrochemical potential called the corrosion potential. This potential is determined by the amount of negative charge is formed when the metal was added to solution (Rehim *et al.*, 2008; Azzeeri *et al.*, 1982). Table 3 shows the value of the free corrosion potential (E_{corr}), corrosion current density (I_{corr}), and resistance polarization (R_p) of the measurement of each sample at various concentration of inhibitor used.

The size of the potential value of corrosion samples indicates a tendency to undergo oxidation on the corrosion media (Cheng *et al.*, 2007; Abdallah, 2004). High and low values on a sample of potential corrosion inhibitor depend on the formation of a protective oxide layer membrane. Solids Fe, Fe_2O_3 , Fe_3O_4 , and $FeO(OH)$ which is a product and serves as a protective corrosion formed according to the reaction:



Products of iron compounds and extracts of cacao peels are frequently referred as passive protective membrane layer impenetrable by oxygen. The stability of the compound Fe_3O_4 is highly dependent on the concentration and temperature of the solution. It needed the higher of corrosion potential enable can damage the

Table 3. Electrochemical and corrosion parameters for mild steel in the absence and presence of *Theobroma cacao* peels extract in NaCl 1,5 M

Inhibitor Conc. (%V/V)	I_{corr} mA cm^{-2}	E_{corr} Vdec^{-1}	ba Vdec^{-1}	bc Vdec^{-1}	R_{p_2} Ωm	IE(%) I_{corr}	IE(%) R_p
Blank	0.06	-0.27	1.80	1.14	7.28	-	-
0,50	0.05	-0.28	3.60	2.80	13.33	18.70	45.39
1,00	0.04	-0.22	6.00	3.75	21.46	25.83	66.70
1,50	0.03	-0.21	5.00	2.50	27.66	29.17	73.69
2,00	0.02	-0.21	5.60	3.20	39.69	68.30	81.65
2,50	0.01	-0.22	4.70	2.25	74.24	85.90	90.19

protective layer. The formation of a protective coating that causes metal corrosion potential shifts towards more positive samples. In theory, if the addition massive element is added in an amount which is not enough in a corrosive medium, there will be an increase in the rate of corrosion due to passivation process. The decrease in corrosion rate can only be reduced if the inhibitor is added until it has reached the minimum concentration for massive metal. If the amount of the minimum concentration for passivation has not been reached, then the protective layer formed could not protect the entire surface of the sample. So that part has a protective oxide coating would be cathodic and parts that are not covered by a protective membrane will be the anodic oxide, thereby increasing the corrosion process on the sample (Vinod *et al.*, 2010; Yetri *et al.*, 2015). The size of the corrosion rate is determined by the polarization resistance value of corrosion and current density, as shown in Fig. 7. In accordance with the mechanism of corrosion which results in the current, when resistant per unit area larger than the current per unit are that occurred small. The increase of resistance polarization on metal surface causes the diffusion of ions and electrons are separated from the metal surface will be

reduced. So that the resulting current is small and the rate of corrosion will be reduced, otherwise the sample has a small values of resistance polarization have a large corrosion rate.

3.4. EIS relationship with inhibitor concentration

The results of EIS measurements on NaCl media at room temperature and atmospheric pressure expressed in the Nyquist plot. Semi-circular Nyquist plot, which shows the relationship between the real impedance to the impedance imaginary. In general, the resulting Nyquist plot does not show the half-circle, but rather a semi-circle. This behavior can be attributed to the frequency dispersion as a result of the electrode surface roughness (Shyamala and Kasthuri, 2012; ASTM G-59-78). The first phase of the impedance measurements is conducted without inhibitor (blank) then it is performed with the addition of inhibitors variation. Nyquist plots difference between the blank and the absence of inhibitors. In the media added inhibitors, an increase the value of impedance in the electrode solution interface, especially R_{ct} value. This shows that the addition of inhibitors inhibit the transfer

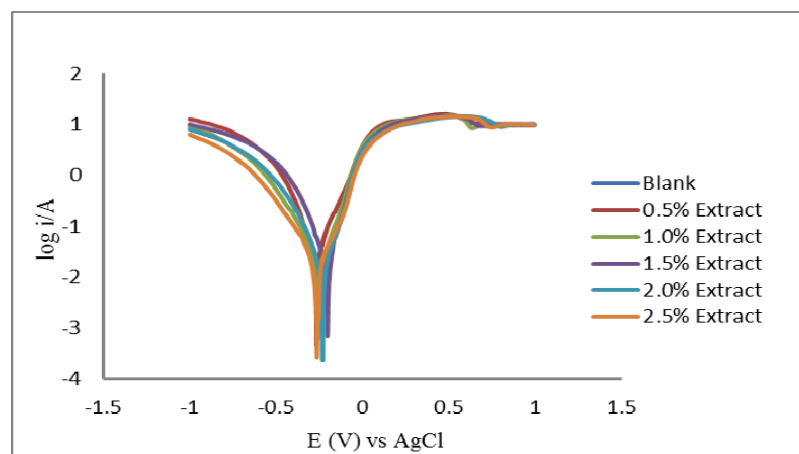
Figure 7. Polarization curves of mild steel absence and presence of *Theobroma cacao* peels extract in NaCl 1.5M

Table 4. Relations inhibitor concentration with the electrochemical parameters in NaCl 1.5M

Inhibitor Conc. (%V/V)	R_s	R_{ct} (Ωcm^2)	Cdl (μFcm^2)	n	EI (%)
0.00	39.30	1080	1.60	0.80	-
0.50	123.00	2660	0.74	0.29	59.40
1.00	44.80	2860	0.27	0.94	62.24
1.50	41.30	3018	0.09	0.83	64.21
2.00	108.00	3489	0.07	1.10	69.05
2.50	836.00	4360	0.06	0.71	75.23

of electrons from the surface of mild steel into the solution. So the process of oxidation of iron atoms and the reduction of H^+ ions are decreasing (Abdallah, 2004; Mohanty and Lin, 2006). Electrochemical parameters on the variation of the inhibitor concentration can be seen in Table 4 and Fig. 8.

3.5. Effect of temperature

Temperature variations have been performed from 303K-323K to see interactions between mild steel and salt absence and presence inhibitors. From Fig. 9 inhibition efficiency increased as the concentration of cacao peels extract increased and it decreased when there was an increasing temperature. The decrease in

inhibition efficiency of the inhibitor as the temperature increased might be due to the adsorption and desorption inhibitors. Adsorption and desorption of inhibitor molecules occurs on a continuous metal surface until a balance between these two processes is reached at a certain temperature.

3.6. Adsorption isotherm

Adsorption of cacao peels extract on the surface of mild steel in NaCl 1.5 M was formulated by using equations 10 (Eddy *et al.*, 2010; Loto *et al.*, 2011).

$$\frac{C}{\Theta} = \frac{1}{K_{\text{ads}}} + C \quad (10)$$

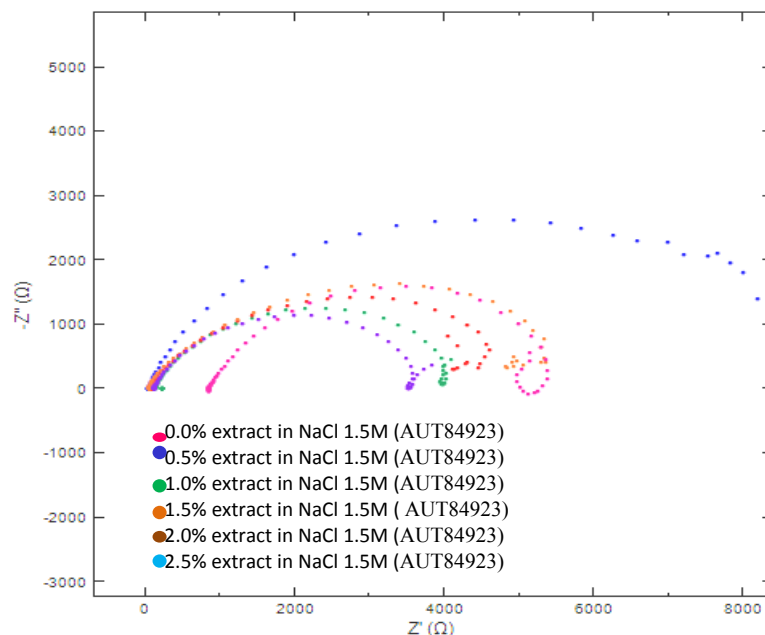


Figure 8. Nyquist plot of mild steel in NaCl 1.5 M media absence and presence of inhibitors of cacao peels extract

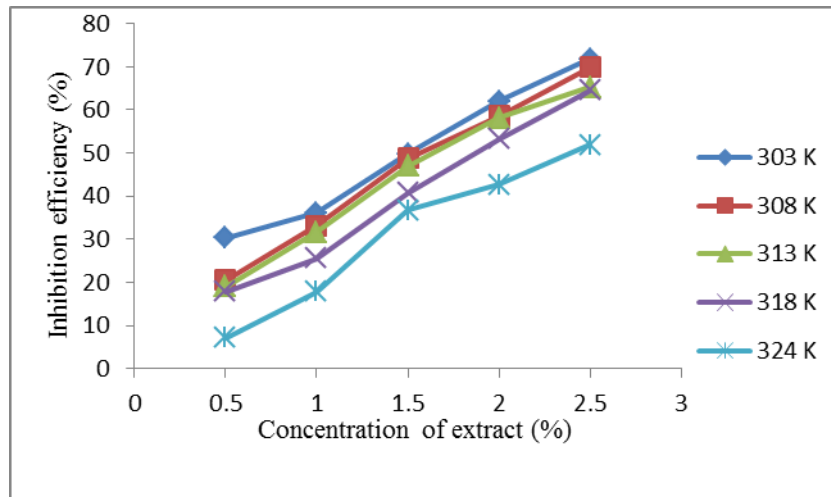
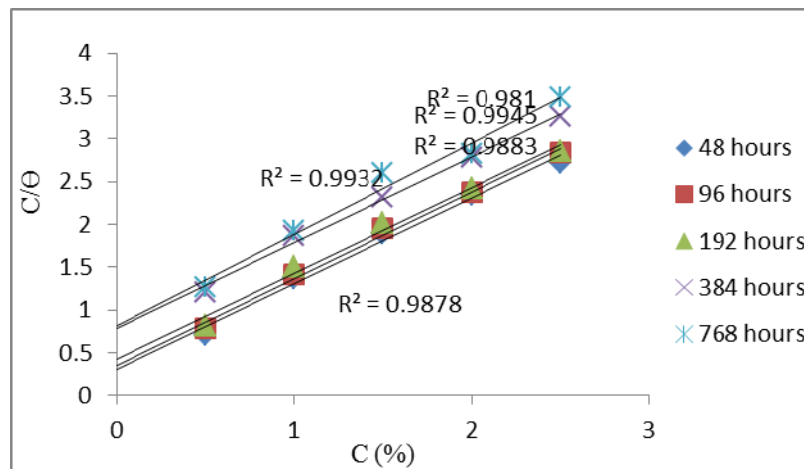
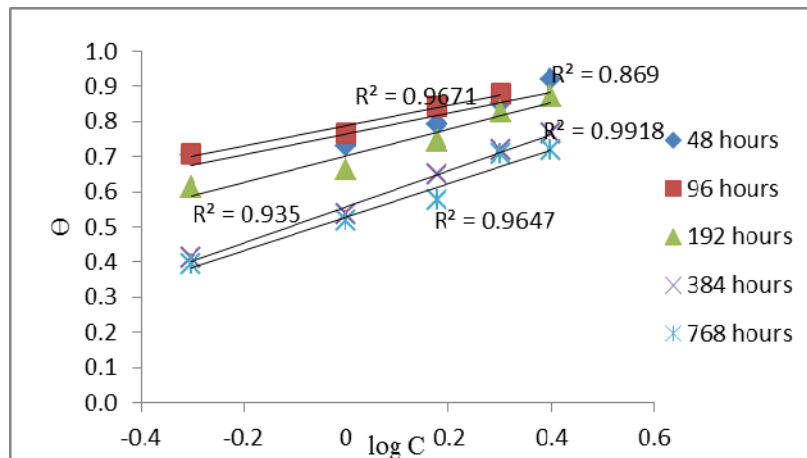


Figure 9. Effect of temperature on Inhibition Efficiency of *Theobroma cacao* peels extract in NaCl 1.5M



(a)



(b)

Figure 10. Isotherm Adsorption (a) Langmuira and (b) Freundlich

Where C is the concentration of inhibitor, K_{ads} is adsorption coefficient, and Θ is surface coverage of mild steel by cacao peels extract. The amount of cacao peels extract covering the steel surface was studied by using Langmuir and Freundlich adsorption isotherm. From 2 isotherm analysis that has been performed, both give a straight line if plotted C/Θ vs C in Fig. 10(a) and 10(b). The highest correlation coefficient that was obtained from the Langmuir adsorption isotherm is 0.98-0.99. The mean value of adsorption occurs closer to the Langmuir adsorption isotherm equation is unimolecular indication.

3.7. Kinetics and thermodynamics

3.7.1. Parameters

To determine the activation energy of corrosion and thermodynamic parameters, weight loss measurements performed from 303 K-323 K absence and presence inhibitors of cacao peels extract in various concentrations. Activation energy on the surface of mild steel in NaCl is determined by using equation 11 (Saratha et al., 2009).

$$k = A \exp \left[\frac{E_a}{RT} \right] \quad (11)$$

Where k is A pre-exponential Arrhenius constant, T is the temperature and R is the ideal gas constant. Arrhenius curve obtained from the plot of $\log V$ vs $1/T$ and $\log V/T$ vs $1/T$ Fig. 11(a) and Fig. 11(b) for the system absence and presence of inhibitors. The activation energy (E_a) and heat of adsorption ΔH is calculated from the slope of the curve in Fig. 11, and the results are presented in Table 5. From Table 5 looks E_a for the process of steel corrosion in NaCl absence inhibitor 98.67 KJmol^{-1} and the presence of inhibitors 100.08 KJmol^{-1} . This value indicates the process of corrosion of mild steel in NaCl with inhibitors occurs slower than without inhibitor. This process occurs because the cacao peels extract to form a passive layer on the surface of mild steel, so the solubility of Fe is reduced (Yetri et al., 2015). The changes of E_a also showed that the inhibitor on the metal surface either participate in the adsorption process. Langmuir adsorption isotherm has provided of the clear mechanism of corrosion inhibition of mild steel surface in NaCl 1.5 M solution absence and presence of the cacao peels extract. Value of the free energy of adsorption (ΔG_{ads}) can be calculated from the following equation 12 (Okafor et al., 2010).

$$K_{ads} = \frac{1}{55.5} \exp \left[\frac{\Delta G_{ads}}{RT} \right] \quad (12)$$

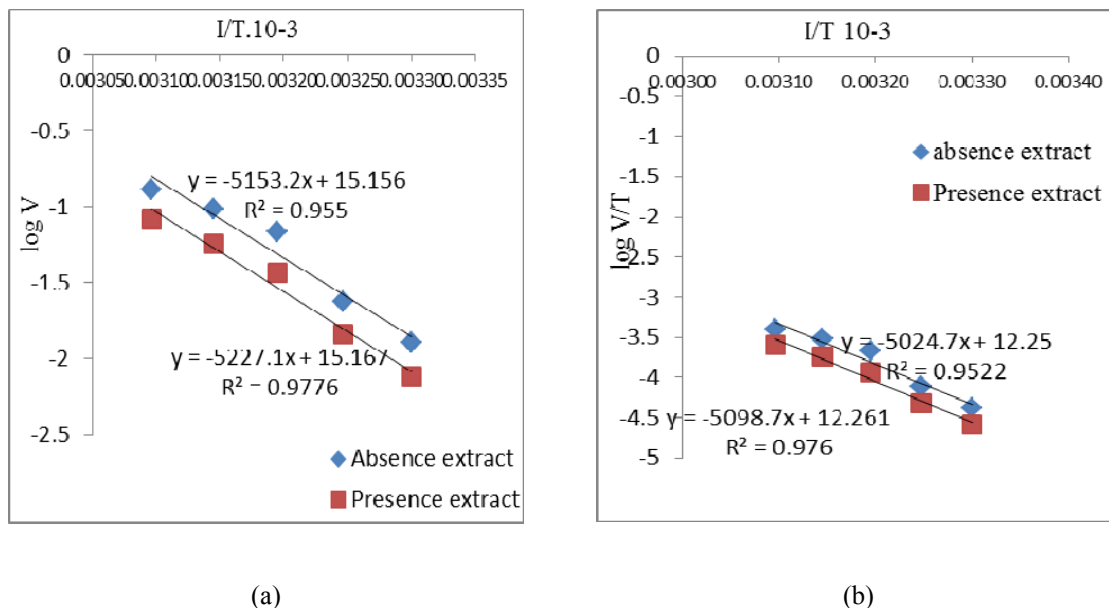


Figure 11. Arrhenius plots for mild steel immersed in 1.5 NaCl solution in the absence and presence of optimum concentration (2.5% v/v) of *Theobroma cacao* peels extract (a) $\log V$ vs $1/T$ and (b) $\log V/T$ vs $1/T$

Table 5. Kinetic and thermodynamic parameters of mild steel in presence and absence of *Theobroma cacao* peels extract in NaCl 1,5 M

Indicator	Ea (kJ/mol)	ΔH (kJ/mol)	ΔG^0 (kJ/mol)	ΔS (kJ/mol)
Blank	98.669	96.109	-	0.317
Blank + inhibitor	100.84	98.293	-17.893	0.562

with R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), the value 55.5 is the concentration of water (H_2O) in solution (mol) and T is the temperature (K). The calculation of value K_{ads} 0.0013 and ΔG_{ads} -17.8386 KJ/mol. Negative values of ΔG_{ads} , indicate adsorption of cacao peels molecules on the surface of mild steel in NaCl spontaneous. Adsorption occurs on the surface of mild steel is chemical, because a large value of ΔH obtained from 20 KJ/mol (Mohanty and Lin, 2006; David and Talbot, 1997).

3.8. Mechanism inhibitors

The presence of the inhibitor molecules on the mild steel surface is due to the adsorption. Adsorption arises due to the adhesion force between inhibitors and the surface of mild steel. The adsorption of inhibitor molecules on the mild steel surface will produce a kind of thin layers (films) that can inhibit the rate of corrosion. In this case inhibitor of cacao peels extract will act as forming a thin layer on the surface of mild steel. Additionally inhibitors also serve as the control of the rate of corrosion by making the metal divider between the media (Loto *et al.*, 2011). Adsorption process of cacao peels extract on mild steel surface will occur in functional group (Hussin and Kassim, 2011; Shyamala and Kasthuri, 2012). The higher the concentration of the inhibitor, which is covered by a piece of metal corrosion inhibitor molecules have also increased as shown in Fig. 6. Bonding that occurs in the process of adsorption inhibitors in mild steel surface are suspected as a covalent bond coordination will produce a complexes compound $\text{Fe}[\text{TCPE}]_6^{+2}$ involving chemical adsorption. This can be seen with the hard layer is removed (Yetri *et al.*, 2015).

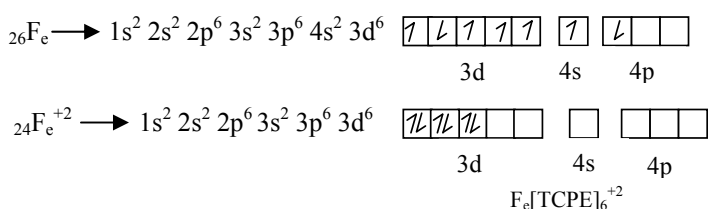
3.9. FTIR analysis

Fig. 12 shows a significant difference between the three spectra. There are several peaks in Fig. 12(a) is lost, but in Fig. 12(b) and 12(c) accompanied by the presence of a new peak in the both picture. However, many peaks that appears in the same or adjacent frequencies. Identified functional groups of cacao peels extract (Fig. 12(a)) is phenols, aromatic rings and ether. Most of these functional groups appear in the corrosion products but with little frequency shift. For example, C-O functional groups that are at a frequency of 1051 cm^{-1} shifted to 1020 cm^{-1} and 1022 cm^{-1} , C=O shift from 1603 cm^{-1} to 1654 cm^{-1} and 1637 cm^{-1} , while the OH shift from 3422 cm^{-1} to 3422 cm^{-1} and 3397 cm^{-1} . New peak appears at frequency 2360 cm^{-1} and 2283 cm^{-1} is the C-H bonds (phenol), 668 cm^{-1} and 835 cm^{-1} is predicted Fe=O bond the effect of strain. These results indicate that there has been interaction and chemical bonding between compounds of extracts cacao peels with metal in surface area. Functional groups identified from existing peaks in both spectra are shown in Table 6.

3.10. Analysis of microstructure

The observation of the surface morphology of mild steel that has not done the treatment and pre- treated with 200x magnification can be seen in Fig. 13(a)-13(c). Photos surface structure of the sample is obtained by using the S-3400N Scanning Electron Microscopy with a magnification of 200 times. Photo initial surface morphology of the specimen can be seen in Fig. 13(a), the image seen the fine lines are white and relatively thin which is the effect of grinding and sanding on the surface of mild steel. Seen also that the surface is flat, clean, and non-porous and there are no holes.

This means it has not been demonstrated mild steel corrosion reaction because there is no influence of the environment such as water, air, acids, salts, bases or from corrosive substances. The morphology of the surface of mild steel after immersion for eight days in NaCl 1.5 M corrosive solution with and without the addition of cacao peels extract shown in Fig. 13(b) and 13(c). Of the two images can be seen there are



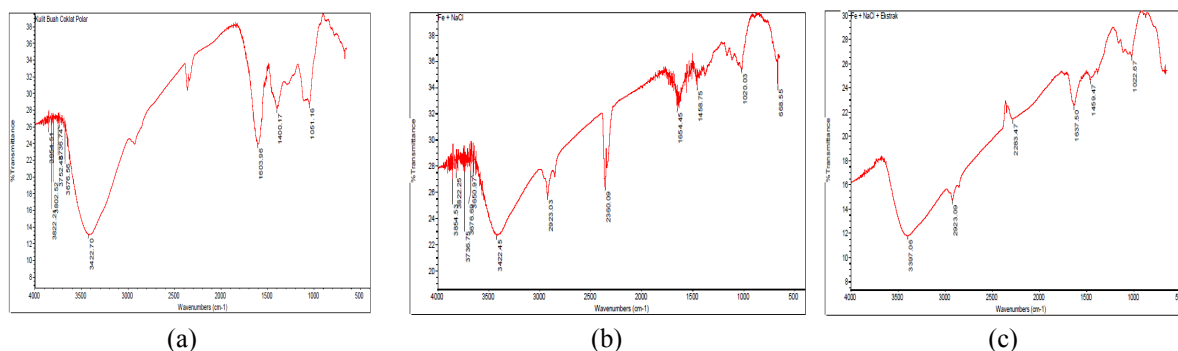


Figure 12. FTIR spectra of (a) TCPE, (b) corrosion product after immersion in NaCl 1.5 M without TCPE for 8 days (196 h) and (c) adsorption layer formed on the mild steel surface after immersion in NaCl 1.5 M with 2.5 % TCPE for 8 days (196 h)

significant differences in the surface of mild steel due to the reaction that occurs in a corrosive solution of sodium chloride. Fig. 13(b) the steel surface looks rough and many clumps of corrosion products. While in Fig. 13(c) with the addition of 2.5% extract visible decrease the rate of corrosion attack, the steel surface is smooth and no visible lumps of corrosion products.

3.11. Analysis of SEM-EDX

Analysis of elements of C and Fe on the surface of mild steel in NaCl 1.5 M was immersed for 8 days with and without the cacao peels extract studied by SEM-EDX. The results of it can be seen in Table 7. Based on the obtained graphs the percentage of element C increases from 0.3% to 6.58% with the cacao peels extract. This proves that C element of the molecule cacao peels extract adsorbed on the mild steel surface to form a passive layer. While the percentage of Fe element decreased in the presence of the cacao peels extracts from 98.79% to 80.00%.

The elements were detected in the initial O in mild steel only does not exist, and in mild steel plus 2.5% extract is detected with a low percentage. While there was an increase oxygen percentage to 15.16% as immersion in NaCl 1.5 M corrosive media without inhibitors, so the oxide formed quickly by an attack from the corrosive ions NaCl. But oxygen percentage is decreased to 14.54% after adding the cacao peels extract. This indicates that the Fe to form complex compounds with molecular cacao peels extract so that the percentage of Fe element were detected becomes smaller (Yetri *et al.*, 2015).

4. Conclusions

4.1. Test results of GC-MS show that the cacao peels extracts contain many secondary metabolites. The functional group of obtained compounds was confirmed by FTIR testing, to determine the heteroatom groups that have great influence in the inhibition of corrosion.

Table 6. FT-IR Transmittance spectra of extract cacao peels, corrosion product and their identification

Peaks from FT-IR spectra, ν (cm ⁻¹)			
TCPE	Corrosion Product without TCPE	Corrosion Product with TCPE	Possible groups
-	-	835	Fe=O
1051	1020	1022	C-O (ether)
1400	-	-	C-C=C(asimetric aromatic)
	1458	1459	C-C (aromatic)
1603	1654	1637	C=O
-	2360	2283	H-C-H (phenol)
	2923	2923	C-H
3422	3422-3854	3397	O-H (phenol)

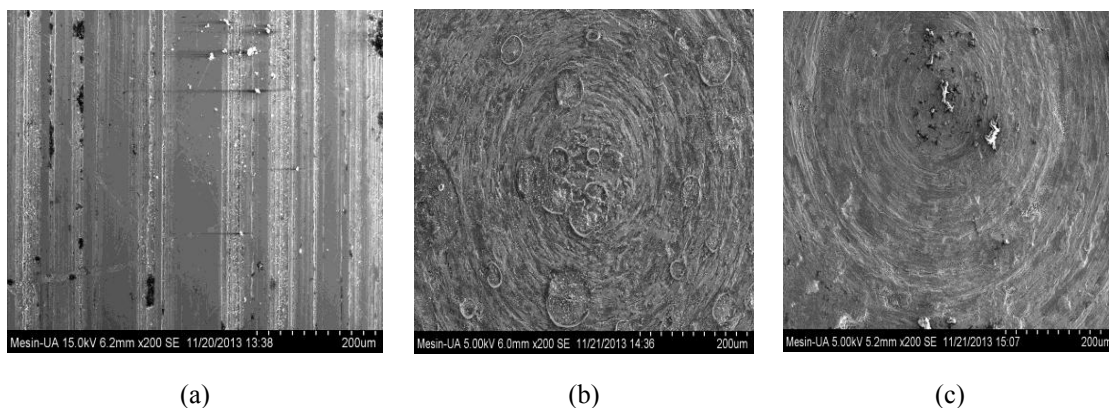


Figure 13. SEM images of Mild steel in NaCl 1.5 M after 8 days immersion at room temperature (a) before immersion (polished), (b) without inhibitor (blank) and (c) with 2.5 % inhibitor.

4.2. The extract of Cacao peels is adsorbed on the surface of the mild steel through chemical adsorption, by coordination covalent bonds with forming a passive layer on its surface. The increasing concentration of the extract, the surface coverage of the mild steel surface increase to.

4.3. The rate of corrosion of mild steel was significantly reduced with the addition of the cacao peels extract in NaCl 1.5 M. But the inhibition efficiency increases with increase in concentration of the extract to 2.5%. Although the efficiency decreases with increasing working temperature, but the efficiency is still high enough until temperature 323 K.

4.4. From the potentiodynamic measurement known inhibitor type cacao peels extract is mixed type inhibitors in NaCl 1.5 M with dominant cathodic inhibitor, obeys Langmuir isotherm adsorption.

4.5. Impedance measurements showed that the addition of inhibitors inhibit the transfer of electrons from the surface of mild steel into the solution, so that the process of oxidation of the iron atoms and the reduction of H^+ ions decreases.

4.6. The mechanism of inhibition between extract of cacao peels with mild steel surface studied through the interaction between pairs of lonely electrons that functions as donor ions to the surface of mild steel as an acceptor.

4.7. It can be concluded that the cacao peels extract is a good corrosion inhibitor for mild steel in NaCl 1.5 M.

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References

Abdallah M. Guar gum as corrosion inhibitor for carbon steel in sulfuric acid solutions. *Portugaliae Electrochimica Acta* 2004; 22: 161-75.

Table 7. Recapitulation of some elements and oxides were identified in the SEM-EDX testing

Treatment	Contain of element (% mass)		
	C	Fe	O
ST 37	0.32	98.79	-
ST 37 + 2.5% extract	6.19	92.66	4.33
ST 37 + NaCl 1.5 M	2.27	80.61	15.16
ST 37 + NaCl 1.5 M + 2.5% extract	6.58	80.00	14.54

- Al-Schaibani H. Evolution of extracts of henna leaves as environmentally friendly corrosion inhibitors for metals. *Materialwissenschaft und Werkstofftechnik* 2000; 31(12): 1060-63.
- ASTM. Standard G. 59-78, Standard practice for conducting potentiodynamic polarization resistance measurements. American Society for Testing and Materials, Philadelphia. 1991; 15-47.
- Azizah AH, Ruslawati NMN, Tee TS. Extraction and characterization of antioxidant from cocoa by-products. *Food Chemistry* 1999; 64(2): 199-202.
- Azzeeri N, Mancina F, Tamba A. Electrochemical prediction of corrosion behaviour of stainless steels in chloride-containing water. *Corrosion Science* 1982; 22(7): 675-87.
- Bouyanzer A, Hammouti B. A Study of anti corrosive effects of Artemisia oil on steel. *Pigment and Resin Technology* 2004; 33(5): 287-92.
- Cheng S, Chen S, Liu T, Chang X, Yin Y. Carboxymethyl chitosan as an ecofriendly inhibitor for mild steel in 1M HCl. *Materials Letters* 2007; 61(14-15): 3276-80.
- David T, Talbot J. Strategies for corrosion control, science and technology. Brian Ralph, CRC Press, New York. 1997; 14-29.
- Eddy NO, Awe F, Ebenso EE. Adsorption and inhibitive properties of ethanol extracts of leaves of Solanum Melongena for the corrosion of mild steel in 0.1 M HCl. *International Journal of Electrochemical Science* 2010; 5: 1996-2011.
- Ferreira JFS, Charles DJ, Wood K, Januck J, Simon JE. A comparison of gas chromatography and high performance liquid chromatography for artemisinin analyses. *Phytochemical Analysis* 1994; 5(3): 116-200.
- Gunavathy N, Murugavel SC. Corrosion inhibition studies of mild steel in acid medium using Musa Acuminata fruit peel extract. *E-Journal of Chemistry* 2012; 9(1): 487-95.
- Hasan SK, Edrah S. Rosemary extract as Eco friendly corrosion inhibitor for low carbon steel in acidic medium. *Journal of Industrial Research and Technology* 2011; 1(2): 110-13.
- Hii CL, Law CL, Suzannah S, Misnawi, Cloke M. Polyphenols in cocoa (Theobroma cacao L.). *Asian Journal of Food and Agro-Industry* 2009; 2(4): 702-22.
- Hussin MH, Kassim MJ. Electrochemical, thermodynamic and adsorption studies of (+)-catechin hydrate as natural mild steel corrosion inhibitor in 1 M HCl. *International Journal of Electrochemical Science* 2011; 6: 1396-414.
- Loto CA. Inhibitor effect of tea (Camellia Sinensis) extract on the corrosion of mild steel in dilute sulfuric acid. *Journal Material and Environmental Science* 2011; 2(4): 335-44.
- Loto CA, Loto RT, Popoola API. Inhibition effect of extracts of Carica Papaya and Camellia Sinensis leaves on the corrosion of duplex (α , β) brass in 1M nitric acid. *International Journal of Electrochemical Science* 2011; 6: 4900-14.
- Loto CA. Electrode potential evaluation of effect of inhibitors on the electrochemical corrosion behaviour of mild steel reinforcement in concrete in H_2SO_4 . *Journal Material and Environmental Science* 2012; 3(1): 195-205.
- Matheswaran P, Ramasamy AK. Corrosion inhibition of mild steel in citric acid by aqueous extract of Piper Nigrum L. *E-Journal of Chemistry* 2012; 9(1): 75-78.
- Mohanty US, Lin KL. Potentiodynamic polarization measurement of Sn-8.5Zn-XAl-0.5Ga alloy in 3.5% NaCl solution. *Journal of the Electrochemical Society* 2006; 153(8): 319-24.
- Noor EA. Temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of Fenugreek leaves. *International Journal of Electrochemical Science* 2007; 2: 996-1017.
- Okafor PC, Ebenso EE, Ekpe UJ. Azadirachta Indica extracts as corrosion inhibitor for mild steel in acid medium. *International Journal of Electrochemical Science* 2010; 5: 978-93.
- Okafor PC, Ebiekpe VE, Azike CF, Egbung GE, Brisibe EA, Ebenso EE. Inhibitory action of Artemisia annua extract and artemisinin on the corrosion of mild steel in H_2SO_4 solution. *International Journal of Corrosion* 2012; Article ID 768729: 1-8.
- Okuda T, Ito H. Tannin of constant structure in medical and food plant, hydrolyzable tannins and polyphenol related to tannins. *Molecules* 2011; 16(3): 2191-217.
- Osman H, Nasarudin R, Lee SL. Extract of cocoa (Theobroma cacao L.) leaves and their antioxidation potential. *Food Chemistry* 2004; 86(1): 41-46.
- Raja PB, Sethuraman MG. Solanum Tuberosum as an inhibitor of mild steel corrosion in acid media. *Iranian Journal of Chemistry and Chemical Engineering* 2009; 28(1): 77-84.
- Rani BEA, Basu BBJ. Green inhibitors for corrosion protection of metals and alloys: an overview. *International Journal of Corrosion* 2012; Article ID 380217: 1-15.
- Rehim SSA, Hazzazi OA, Amin MA, Khaled KF. On the corrosion inhibition of low carbon steel in concentrated sulphuric acid solutions. Part 1: chemical and electrochemical (AC and DC) studies. *Corrosion Science* 2008; 50(8): 2258-71.
- Samuel A. Corrosion and stress corrosion behavior of low and medium carbon steel in agro-fluid media. *Leonardo Electronic Journal of Practice and Technologies* 2007; 10: 55-66.
- Saratha R, Priya SV, Thilagavathy P. Investigation of Citrus aurantiifolia leaves extract as corrosion inhibitor for mild steel in 1 M HCl. *E-Journal of Chemistry* 2009; 6(3): 785-95.
- Sastri VS. Green corrosion inhibitor theory and practice. John Wiley & Sons, Inc. Publication, Canada. 2011; 103-212.
- Shyamala M, Kasthuri PK. The inhibitory action of the extracts of Adathoda vasica, Eclipta alba, and Centella asiatica on the corrosion of mild steel in hydrochloric acid medium: a comparative study. *International Journal of Corrosion* 2012; Article ID 852827: 1-13.

Vinod KKP, Narayanan PMS, Thusnavis GR. Pericarp of the fruit of *Garcinia Mangostana* as corrosion inhibitor for mild steel in hydrochloric acid medium. *Portugaliae Electrochimica Acta* 2010; 28(6): 373-83.

Yetri Y, Emriadi, Jamarun N, Gunawarman. Corrosion inhibitor of mild steel by polar extract of *Theobroma cacao* peels in hydrochloric acid solution. *Asian Journal of Chemistry* 2015; 27(3): 875-81.

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