Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(5):1083-1094

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Corrosion inhibition of environmental friendly inhibitor using *Theobroma cacao* peels extract on mild steel in NaCl solution

Yuli Yetri[1*], Emriadi[2], Novesar Jamarun[2] and Gunawarman[3*]

[1]*Department of Mechanical Engineering, Padang State Politechnic, Limau Manis, Padang, Indonesia*
[2]*Department of Chemistry, Andalas University, Padang, Indonesia*
[3]*Department of Mechanical Engineering, Andalas University, Padang, Indonesia*

ABSTRACT

The effects of Theobroma cacao peels extract (TCPE) on corrosion inhibition of a 0.32%C mild steel in 1.5M NaCl solution was studied using weight loss at various temperature, and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods at room temperature and elevated temperature. Electrochemical polarization was conducted to evaluate the type of inhibition. Infrared spectra and phytochemicals test were performed to determine the chemicals constituent in the extract of cacao peels that play 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). Experimental results revealed that the corrosion rate decreases with increasing extract concentration, but it increases with increasing temperature. The maximum corrosion inhibition efficiency is relatively high, that is 91.93% (weight loss), 85.90% (Tafel), 90.19% (Rp) and 75.23% (EIS) at a concentration of 2.5% the extract. The increasing of inhibition efficiency is due to the increase of charge resistance transfer (Rct) as a result of chemical adsorption in the surface. Chemical adsorption occurs on the surfaces obeys Langmuir isotherm adsorption, with an indication of adsorption unimoleculer. The polarization curve shows the inhibitor behaves as a mixed inhibitor with the dominant cathodic inhibition. The use of polar extract of Theobroma cacao peels as inhibitor is quite effective in reducing corrosion attack of NaCl solution on the mild steel.

Key word: *Theobroma cacao* peels extract (TCPE), Corrosion inhibitor, NaCl, Corrosion rate, Mild steel

---

INTRODUCTION

It is well known that corrosion is a natural process that occurs easily on mild steel to form a chemical compound that leads to degradation of the material. However, mild steel still have a high popularity in the market because they have ability to be used in a wide variety of needs, easily welded and relatively inexpensive. Steel has been then widely used as a commercial commodity to make construction, automotive, machinery, automobile industry etc. The main focus of steel research works up to now, therefore, how to improve its low corrosion resistant to make it inadequate for exposuring in acid and aggressive salt such as hydrochloric acid and natrium chloride, respectively [1-3]. Steel corrosion starts spontanuosly when they come in contact with sea water in the presence of air. The corrosion processes then progress quickly after disruption of the protective barrier and accompanied by number of reaction which change the composition and properties of both steel surface and the local environment[1]. The steel, therefore, needs maintenance to reduce the corrosion rate.

There are several ways to slow the corrosion rate, namely coating, anodic or cathodic protection and the addition of inhibitor [1-4]. Inhibitor corrosion treatment is one of the most efficient and economical, because it can form a protective layer in the surface of the steel. Inorganic inhibitor is common widely used inhibitor substance up to now. However, the use of the conventional inorganic inhibitors has a negative impact because of its toxicity and non-biodegradable [5]. Therefore, it may be advisable for using organic inhibitors from natural products. Such inhibitor is non-toxic and biodegradable, and it is categorized as a enviromental friendly inhibitors [5, 6].

There are many kind of environmentally friendly corrosion inhibitors developed worlwide up to now. Some of them is extracted from bark, skin fruit, leave, and seeds, such as *musa aquapinata* skin [3], henna leaves [4], *azadirachta indica* [7], kalmegh leaves [8], rosemary flower [9] , *citrus aurantifiifolia* [10], *carica papaya* leaves [11], *piper* ningrum [12], a*rtemisia* annua [13], *garcinia mangostana* fruit [14], and fenugreek leaves [15]. Recently, we have developed an environmentally friendly corrosion inhibitor using *Theobroma cacao peels extract* [1]. The result showed that such extract is very effective to inhibit corrosion rate of mild steel in hydrochloric acid environment. Since mild steel is also used widely in marine environment, it is also interesting to investigate the inhibitory power of this cacao peels extract in a sodium chloride solution. This paper reports the inhibition behavior of *Theobroma cacao* peels extract (TCPE) and its effect on the corrosion rate of mild steel in NaCl 1.5M environment using some corrosion test methods.

EXPERIMENTAL SECTION

Mild Steel Preparation

Material used for this study was a mild steel plate that is commonly used as construction material. Chemical composition of the plate, determined by a Foundry-Master Xpert Spectrometry, is a medium carbon steel with carbon content of 0.32%. The composition of main elements is shown in detail in Table 1. Corrosion test specimens were a coin form with a diameter of 25 mm and a thickness of 2-3 mm.

The specimens were polished using emery paper to the size of fineness #120, 600, 800, 1000, 1500, and 2000. They then washed with detergent and distilled water, and rinsed with alcohol to remove any contaminants. The specimens were subsequently dried with a hot dryer at a temperature of 30°C for 10 minutes, and finally stored in desiccators.

Table 1. Chemical composition of mild steel sample

Chemical Composition (% mass)								
C	Si	Cr	Mo	Mn	S	Cu	P	Fe
0.32	0.22	0.1	0.2	0.9	0.06	0.3	0.07	Balanced

Cacao Peels Extract Preparation

Cacao peels were collected from a cacao plant in Pariaman, West Sumatera, Indonesia. They were then cleaned, chopped into small pieces, and dried in the air without sunlight for 14 days. They were subsequently milled into powders. Cacao peel powders of 200 grams were then put in macerator, and added with in 1 L methanol 70%. The mixture was stirred and left in a macerator for 4-5 days. Maceration results were 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 to get a concentrated extract. This concentrated extract was finally used as inhibitors corrosion.

Phytochemicals Identification and Fourier Transform Infra Red Spectroscopy (FT-IR)

It order to determine chemichal composition and the type of bonding for organic inhibitor adsorbed on the metal surface, phytochemicals identification and Fourier Transform Infra Red Spectroscopy (FT-IR) tests, respectively, were carried out. It has been established that FTIR spectrophotometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface. Phytochemicals examination was performed to determine the major constituents of *Theobroma cacao* peels extract (TCPE) by using certain chemical reagent. Functional groups of *Theobroma cacao* peels extract were identified by using a Nicolet iS10-FTIR spectrophotometer with KBr disk. The working frequency ranges from 4000 to 400 cm^{-1}. The spectra were analyzed by using a related compound functional group table.

Weight Loss Method
Each specimen was weighed to determine the initial weight, and then immersed into NaCl 1.5M medium for 48, 96, 192, 384, and 768 hours. The inhibitor concentration variation was selected as much as 0.5, 1.0, 1.5, 2.0 and 2.5% mass. After exposuring for each predetermined time, corrosion products were then removed from the media, brushed them using a soft brush, washed with distilled water and finally rinsed with acetone. The specimens were dried at room temperature, and then weighed again to obtain final weight. Corrosion rate and inhibition efficiency were calculated using related equations [1].

Potentiodynamic Polarization Study
A computer controlled potentiostat instrument EDAQ 466 Potentiostat-Advanced Electrochemical System was used in this study. The mild steel samples was put on holder footage of the equipment, and dipped in a corrosion cell containing a solution of 10 ml corrosive media. The mild steel sampel was put as the working electrode. While, platinum and AgCl was put as auxiliary electrode and counter electrode, respectively. The three electrodes were then connected to the potentiostat instrument. The results of measurements include the corrosion current density (Icorr), corrosion potential (Ecorr), and resistance polarization (Rp). This parameter was then employed to calculate the inhibition efficiency using using Tafel plots [1].

Corrosion testing using the technique of Resistance Polarization is intended to determine the sample resistance during oxidation when external potential is applied to the system. The resistance polarization is a good method to determine the corrosion rate and inhibition efficiency without damaging the metal by using the following equation [16].

$$Rp = \frac{ba \times bc}{Icorr x\, 2.303\, (ba + bc)} x100\% \quad (1)$$

Where: b_a = anodic Tafel slope, b_c = cathodic Tafel slope, I_{corr} = corrosion current densities and Rp = resistance polarization

Electrochemical Impedance Spectroscopy (EIS) Study
EIS method was used to determine the resistant transfer of electric charge on the layer interface between the solution and mild steel surface. EIS spectra were recorded by Potentiostat/Galvanostat AUTOLAB PGSTAT 302N. The procedure for this method is almost the same as the Tafel method in accordance to ASTM G59-78[23]. Electrochemical parameter obtained from this test is Rs, Rct and Cdl, where Rs is the resistance of the solution, the Rct is the charge transfer resistant and Cdl is the capacitance of the electric double layer. Initial operation of the tool is tested by OCP (open circuit potential) to determine the stability of the electrode surface and the test solution. A peak amplitude of 10 mV with a frequency range of 0.1 Hz to 100Hz was used during EIS measurement. The percentage efficiency inhibition is determined by the following equation 2 [16-17]:

$$\%EI = \frac{Rct_{inh} - Rct}{Rct_{inh}} x100\% \quad (2)$$

Where, Rct and Rct (inh) are the charge transfer resistant of mild steel in solutions without and with the presence of inhibitors.

Surface Analysis
Surface samples were analyzed using Hitachi S-3400N Scanning Electron Microscopy. This observation aims to observe the change of sample surfaces before and after the occurrence of corrosion.

RESULTS AND DISCUSSION

Extract and Corrosion Product Compositions
Phytochemicals examination of *Theobroma cacao peels extract* show that the extract contains flavonoid, phenolic, alkaloid, terpenoid and steroid and alkaloid, etc with the main identified constituents are phenolic and alkaloid. This compounds are containing heteroatom group that act as a corrosion inhibitor [1].

Table 2. FTIR transmittance spectra of extract cacao peels, corrosion product and their identification

Peaks from FTIR spectra, ν (cm^{-1})			Possible groups
Theobroma cacao peels extract	Corrosion Product without Theobroma cacao peels extract	Corrosion Product with Theobroma cacao peels extract	
-	-	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)

The reflectance FTIR spectra is then used to know exactly the corrosion inhibition of mild steel in such media. FTIR spectra of the TCPE extract, corrosion product without extract and with extract show that there is a significant difference between the three spectra as shown in Fig. 1(a), (b) and (c), respectively. There are several peaks unappear, but in Figure. 1(b) and 1(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 (Figure. 1a) is phenol, aromatic rings and ether. Most of these functional groups appear in the corrosion products but with a little frequency shift. For example, C-O functional groups that are at a frequency of 1051cm^{-1} shifted to 1020 and 1022 cm^{-1}, C = O shift from 1603 cm^{-1} to 1654 cm^{-1} and 1637, while the OH shift from 3422 cm^{-1} to 3422 cm^{-1} and 3397. New peak appears at frequency 2360 and 2283 is the C-H bonds (phenol), and another new peak at 835 cm^{-1} is predicted Fe=O bond the effect of strain. This result indicates that there has been interaction and chemical bonding between compounds of extracts cacao peels with metal in surface area. List of functional groups that is identified from the existing peaks in the both spectra is shown in Table 2. This result indicates that the corrosion inhibition of TCPE in NaCl 1.5M solution is due to the adsorption of extracts constituents on the mild steel surface.

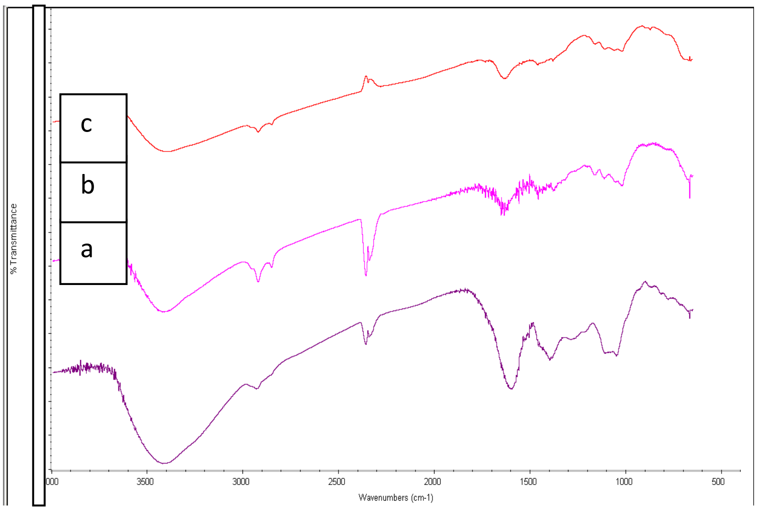


Figure 1. FTIR spectra of a) Theobroma cacao peels extract b) corrosion product after immersion in NaCl 1.5M without Theobroma cacao peels extract for 8 days (196 h), and c) adsorption layer formed on the mild steel surface after immersion in NaCl 1.5M with 2.5 % Theobroma cacao peels extract for 8 days (196 h)

Effect of Concentration on Corrosion Rate

The result of the corrosion rate and corrosion efficiency calculations is shown in Figure. 2. It can be seen that, the increase in the concentration of extract decreases corrosion rate, and then, therefore, increases the efficiency of inhibition. The increase of inhibition efficiency is also followed by an increase in surface coverage (θ), because the both formula is actually the same, where the formula of surface covarage without percentage. This means the increase in exact concentration increases the number of inhibitor molecules adsorbed on the steel surface and reduces the area of surface that is available for the direct ion attack.

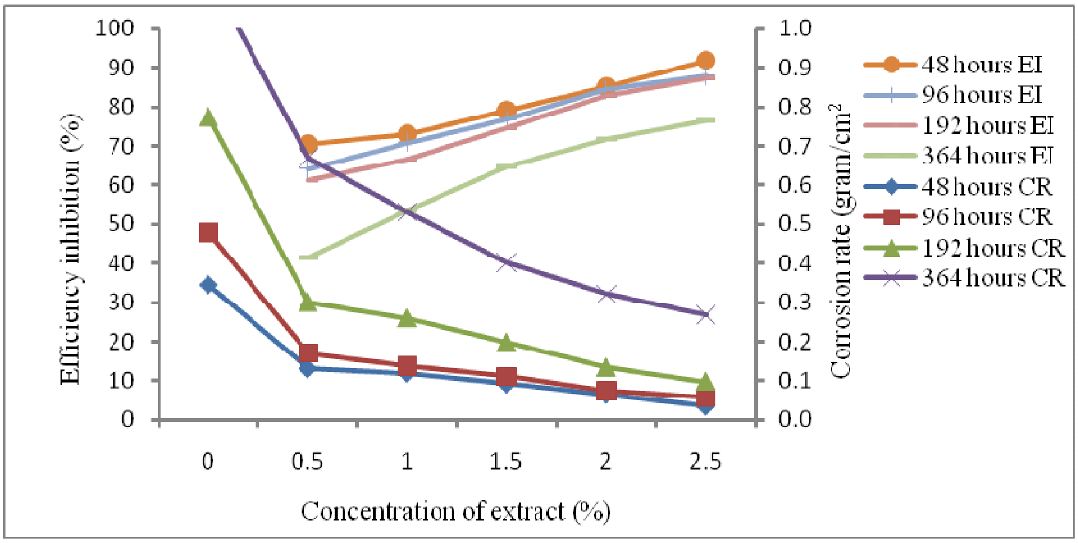


Figure 2. The effect of concentration of extract on efficiency inhibition and corrosion rate at different time

The inhibitive effect of *Theobroma cacao* peels extract (TCPE) is ascribed to the presence of organic compound in the extract. TCPE contain several organic compound of high molecular weight with heteroatom with lonely electron pairs in their molecules [1,8]. These include flavonoid, phenolic, alkaloid, terpenoid and steroid and alkaloid. The presence of such organic compounds in TCPE is responsible for decreasing corrosion rate. It is needed a further investigation to know which one of the compounds has significant effect. However, previous works [1]' suggests that phenolic plays a dominant role to control corrosion rate. This compound has many rich heteroatom groups with free electron pairs which can be donated to form bonds at the surface of mild steel.

The inhibition efficiency of TCPE is found slightly better than that of *Vernonia amygdalina* extract [16]. The inhibition efficiency of such kind extract of small shrub that grows in the tropical Africa is less than 75% in the solution of NaCl 3.5% . This is may due to the different of inhibition mechanism among them. The mechanism of inhibition of *Vernonia amygdalina* extract by physical adsorption, and TCPE inhibition mechanism is by chemical adsorption. In physical adsorption, molecular bonding is a Van der Waals bound or electrostatic force, and this bond is easily dislodged. While the chemical adsorption of molecules bound is a chemical bond with the transfer or sharing of content, so this bond is difficult to be destroyed, and thus, it is able to protect mild steel from chloride ion attack. This work suggests that both adsorption types can be formed on the surface of mild steel to form a film layer that can inhibit the corrosion reaction depend on the content and concentration of corrosion media.

The increase of surface coated mild steel by the cacao peels extract is quite proportional with efficiency of inhibition as the result of the increase of the surface contact of the sample with the solution [1-2]. The occurrence of surface coating, in accordance with the protection mechanism, is that the natural extracts are compounds containing atoms with lone electron pairs [10]. These atoms act as electron donors that produce complexes with iron [18]. These complexes are stable, and it is not easily oxidized and envelop the iron metal surface, so that the rate of corrosion can be inhibited.

Electrochemical Measurement Results

Typical potentiodynamic polarizing curve showing the inhibitory action of *Theobroma cacao peels* extract in NaCl 1.5M is shown in Figure 3. The corrosion parameters such as E_{corr}, I_{corr}, Tafel slope constants (b_a and b_c), linear polarization resistance (R_p), that is obtained from this curve, is presented in Table 3 where Ecorr is the value of the free corrosion potential, Icorr is the corrosion current density (Icorr), and Rp is the resistance polarization of each sample at various concentration of inhibitor. I_{corr} decreases with decreasing extract concentration. This confirms the inhibitory action of *Theobroma cacao* peels extract on metal surface. It can be seen that E_{corr} value has not been shifted to any particular direction as compared to the blank one, which indicates that the inhibitor acts through mixed mode of inhibition. Tafel slopes b_a and b_c obtained in the presence and absence of the *Theobroma* *cacao* peels extract revealed that evolution mechanism is strongly affected by the presence of the inhibitor, and, thus corrosion of mild steel is under mixed control in both anodic dissolution and cathodic hydrogen. It can be also said that *Theobroma cacao peels extract* acts as a mixed type inhibitor in this media. The increase in R_p values with increase in concentration of inhibitor indicates the effectivity of inhibition. Thus, the inhibition efficiency, which is calculated by polarization technique, increases with increasing extract concentration.

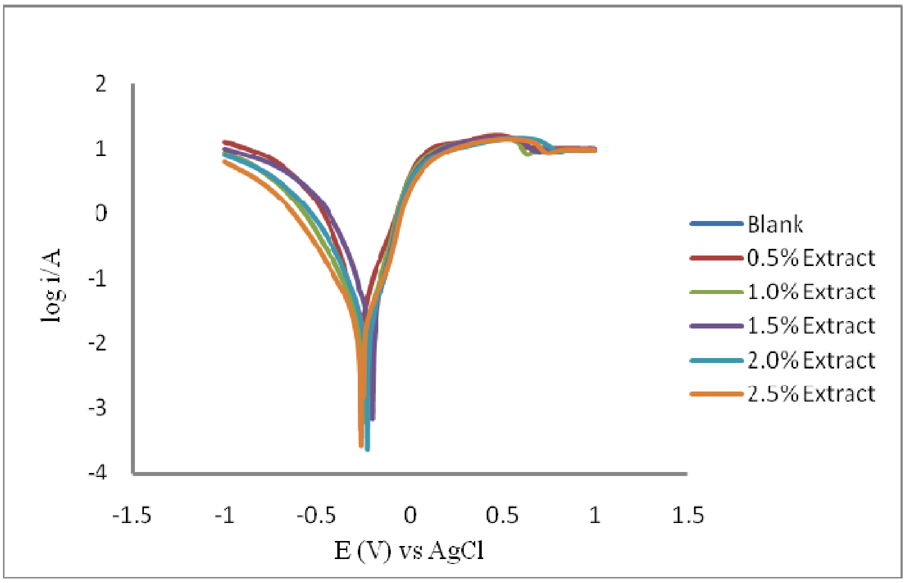


Figure 3. Polarization curves of mild steel in NaCl 1.5M in the absence and presence of *Theobroma cacao peels* extract

As the metal is inserted into the solution, interfacial electrochemical reaction between the metal and the solution occurs. 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 [19-20].

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

Inhibitor Conc. (%V/V)	I_{corr} $mAcm^{-2}$	E_{corr} $Vdec^{-1}$	b_a $Vdec^{-1}$	b_c $Vdec^{-1}$	Rp Ωcm^2	EI(%) I_{corr}	EI(%) Rp
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	0.05	-0.22	6.00	3.75	21.46	25.83	66.07
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	39.67	68.30	81.65
2.50	0.01	-0.22	4.70	2.25	74.24	85.90	90.19

The obtained corrosion potential value of mild steel indicates a tendency of oxidation reaction as commonly observed at the surface of the steel [19, 21]. Low value on a potential corrosion inhibitor in the samples indicates that a formation of a protective oxide layer [15,20], where the present of oxide layer decreases the potential. Theoritically, solid Fe, Fe_2O_3, Fe_3O_4, and FeO(OH) which is a corrosion product and serves as a corrosion, formed according to the reaction [22]:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^- \quad (3)$$

$$2Fe(OH)_2^{+2} + Fe^{+2} + 2H_2O \rightarrow Fe_3O_4 + 6H^+ \quad (4)$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \quad (5)$$

$$Fe(OH)_2^+ + OH^- \rightarrow FeO(OH) + H_2O \quad (6)$$

The TCPE has a function to inhibit this reaction, and thus protect the mild steel from the succesive reaction. Corrosion products and extracts of cacao peels more often referred to as a 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 is needed the higher of corrosion potential enable can damage the protective layer. The formation of a protective coating layer causes metal corrosion potential shifts towards to be more positive [15, 23]. The addition a massive solid element in a corrosive medium will decreases the corrosion rate due to passivation process. The decrease in corrosion rate can only be achieved if the inhibitor added has reached the minimum concentration. As 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 [19-20].

The corrosion rate, which is determined by the polarization resistance value of corrosion and current density, is shown in Table 3. In accordance to the mechanism of corrosion when resistant per unit area is large, the current per unit area is small. The increase of resistance polarization on metal surface, therefore, causes the diffusion of ions and electrons are separated from the metal surface will be reduced. So that the resulting of current is small and the rate of corrosion will be reduced**.** This proves that the presence of protective layer in the surface of the sample.

Impedance Measurement

The effects of the inhibitor concentration on the impedance behavior of mild steel in NaCl 1.5 M corresponding to Nyquist plots, is shown in Figure 4. The Inhibition Efficiency persentation at different inhibitor concentration is calculated by using the following Equation 2.

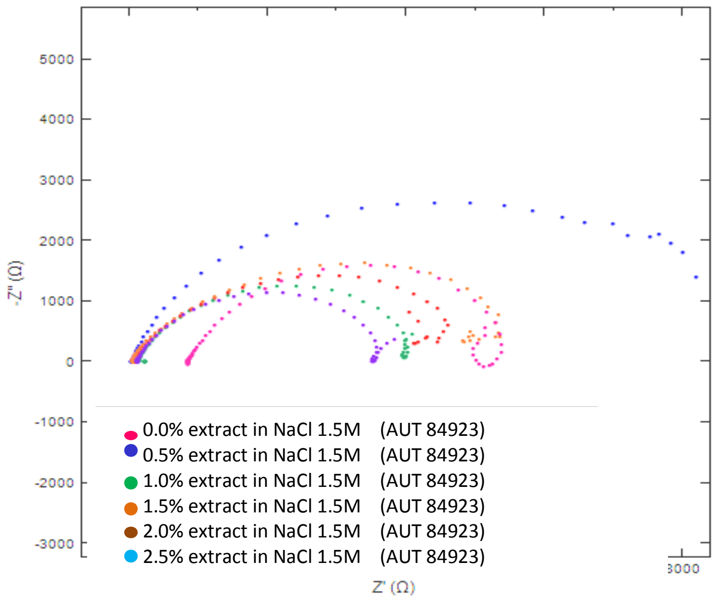


Figure 4. Nyquist plot of mild steel in NaCl 1.5M media in the absence and presence of inhibitors of cacao peels extract

Table 4. Effect of inhibitor concentration on the electrochemical parameters in NaCl 1.5M

Inhibitor Conc. (%V/V)	Rs	Rct (Ωcm^2)	Cdl ($\mu F cm^2$)	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

The lower capacitance (C_{dl}) values for NaCl 1.5 M medium indicates the in homogeneity of surface of the metal roughened due to corrosion. The C_{dl} values decreases on increasing the inhibitor concentration and reaches very low value for the optimum concentration of all the studied systems indicating that the reduction of charges accumulated in the double layer due to formation of adsorbed inhibitor layer [15,24]. The charge transfer resistance (R_{ct}) of double layer increases with increasing the concentration of the inhibitor up to the optimum level indicating the decrease of corrosion rate [19-20].

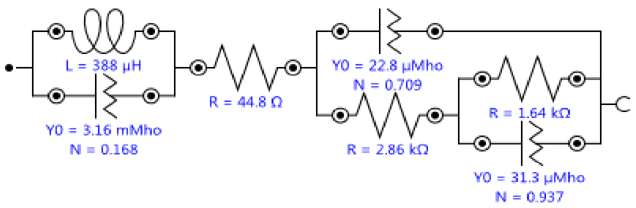


Figure 5. The equivalent circuit model used to fit the experimental result for extract 2,5%

Effect of Temperature

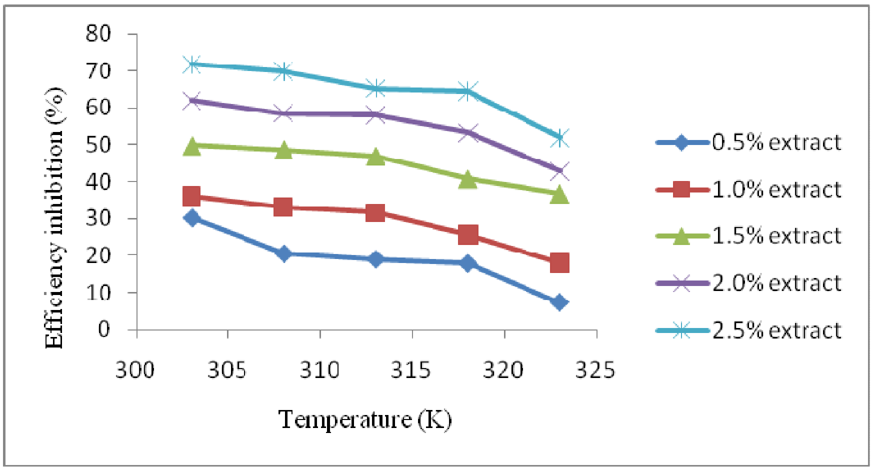


Figure 6. Effect of temperature on Efficiency Inhibition of *Theobroma cacao peels* extract different of concentration of extract in NaCl 1.5M

Kinetics and Thermodynamics Parameters

In order to determine the activation energy of corrosion and thermodynamic parameters, weight loss measurements were performed at the temperature of 303-323 K with the absence and presence of inhibitor. Activation energy on the surface of mild steel in NaCl is determined by using following equation 7 [12,14].

$$\log V = \log A + Ea/RT \qquad (7)$$

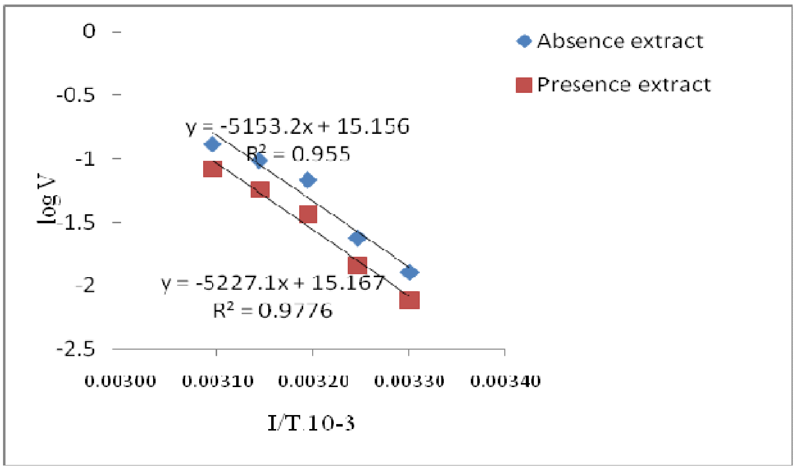
Where k is a pre-exponential Arrhenius constant, T is the temperature and R is the ideal gas constant. Arrhenius curve obtained from the plot of log V vs 1/T and log V/T vs 1/T Figure 8a and Figure 8b for the system with and without inhibitors. The activation energy (Ea) and heat of adsorption ΔH was calculated from the slope of the curve in Figure 7, and the results are presented in Table 5. It can be seeen that Ea for the process of steel corrosion in NaCl without inhibitor is 98.67 $KJmol^{-1}$ and with the presence of inhibitors is 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 [1,25]. The changes of Ea also showed that the inhibitor on the metal surface either participate in the adsorption process. Langmuir adsorption isotherm has provided a clear of the mechanism of corrosion inhibition of mild steel surface in NaCl 1.5M solution without and with the presence of the extract. Value of the free energy of adsorption (ΔG_{ads}) can be calculated from the following equation 8 [8-10].

$$K_{ads} = \frac{1}{55.5} exp\left[\frac{-\Delta G_{ads}}{RT}\right] \qquad (8)$$

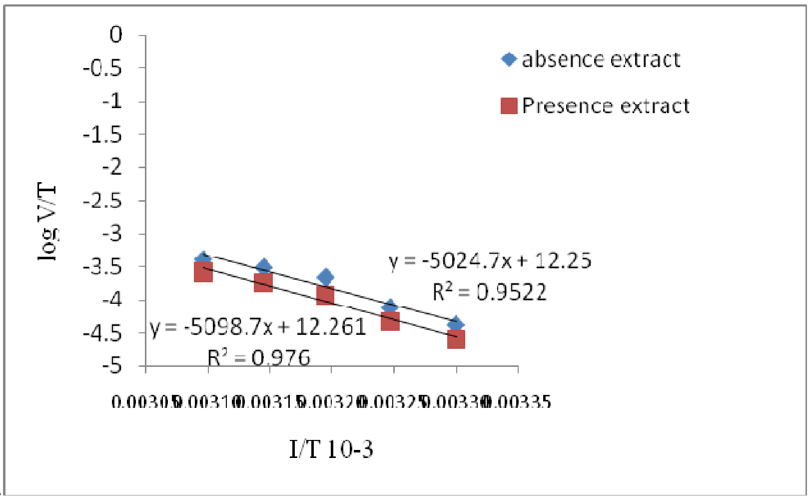
With R is the ideal gas constant (8.314 $Jmol^{-1}K^{-1}$), the value 55.5 is the concentration of water (H_2O) in solution (mol) and T is the temperature (K). The calculation of value K_{ads} 0.0013 and ΔG_{ads} -17.8386 KJ/mol. Negative values of ΔG^o, indicate adsorption of cacao peels molecules on the surface of mild steel in NaCl spontaneous**.** Adsorption occurs on the surface of mild steel is chemical, because the obtained value of ΔH is larger than 20 KJ/mol [14].

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

No	Indicator	Ea (kJ/mol)	ΔH (kJ/mol)	ΔG^o (kHz/mol)	ΔS (kHz/mol)
1.	Blank	98.67	96.11	-	0.32
2.	Blank + inhibitor	100.84	98.29	-17.84	0.56



(a)



(b)

Figure 7. Arrhenius plots for mild steel immersed in NaCl 1.5M solutions in the absence and presence of optimum concentration (2.5 % v/v) of *Theobroma cacao peels extract* (a) log V vs 1/T (b) log V/T vs 1/T

Surface Morphology

The observation of the surface morphology of mild steel before and after immersing the treatment and pre-treatment is shown in Fig. 8a-8c. Initial surface morphology of the specimen can be seen in Figure. 8a, the image seen the fine lines are white and relatively thin which is the effect of grinding on the surface of mild steel. It can be 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 1.5M corrosive solution with and without the addition of cacao peels extract shown in Figure 8b and 8c. From the two images can be seen there are significant differences in the surface of mild steel due to the reaction that occurs in a corrosive solution of sodium chloride. Fig. 8b the steel surface looks rough and many clumps of corrosion products. While in Fig. 8c 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.

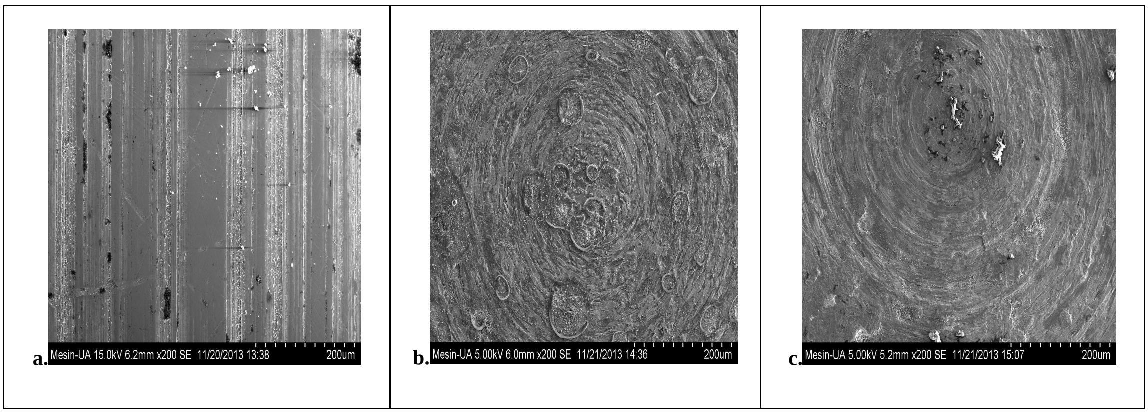


Figure 8. SEM images of Mild steel in NaCl 1.5M after 8 days immersion at room temperature (a) before immersion (polished) (b) without inhibitor (blank) (c) with 2.5 % inhibitor

Chemicals Composition on the Surface

Analysis of elements of C, O and Fe on the surface of mild steel in NaCl 1.5M after immersion for 8 days with and without the presence of cacao peels extract is shown in Table 6. Based on the obtained graphs the percentage of element C increases from 0.30% 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 does not exist, and another analysis is detected with a low percentage. While there was an increase in oxygen percentage to 15.16% as immersion in NaCl 1.5M 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.

Table 6: Recapitulation of some elements and oxides were identified in the SEM-EDX testing

No	Treatment	Contain of element (% mass)		
		C	Fe	O
1.	ST 37	0.32	98.79	-
2.	ST 37 + extract 2.5%	6.19	92.66	2,33
3.	ST 37 + NaCl 1.5M	2.27	80.61	17.16
4.	ST 37 + NaCl 1.5M + extract 2.5%	5.58	80.00	14.54

Adsorption Isotherm

Adsorption of cacao peels extract on the surface of mild steel in NaCl by using Langmuir equations [1,8] is shown in Figure 9. The highest correlation coefficient is obtained from the Langmuir adsorption isotherm that is 0.98-0.99. It means that adsorption occurs closer to the Langmuir adsorption isotherm equation is unimoleculer.

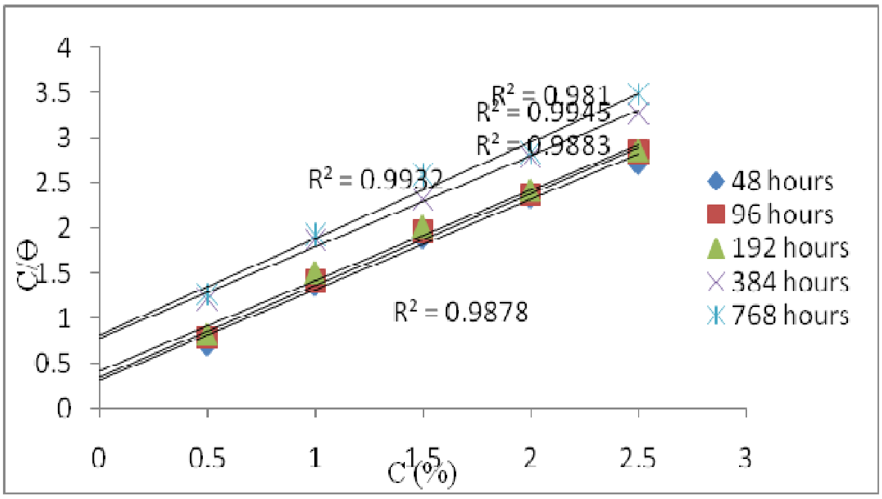


Figure 9. Isotherm Adsorption Langmuir

Mechanism of Inhibition

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 functional group the surface of mild steel [1]. Additionally inhibitors also serve as the control of the rate of corrosion by making the metal divider between the media [8, 26]. Adsorption process of cacao peels extract on mild steel surface will occur in solution**.** The higher the concentration of the inhibitor, which is covered by a piece of metal corrosion inhibitor molecules have also increased because efficiency inhibition increase to as shown in Fig. 2. Atomic bonding that occurs on inhibitor adsorption processes in mild steel surface alleged coordination covalent bonds involving chemical adsorption as seen in the hard layer is removed [1, 25]. Adsorption compounds found in the cacao peels extract will produce a ferro complexes compound $Fe[TCPE]_6{}^{+2}$ as can be seen in Figure 10.

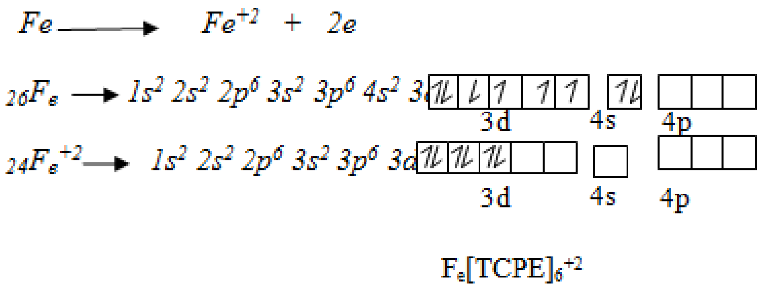


Figure 10. Mechanism of complexes compound between metal and TCPE inhibitor

CONCLUSION

1. Inhibition efficiency increases with increasing extract concentration with maximum efficiency is relatively high, that is 91.93% (weight loss), 85.90% (Tafel), 90.19% (Rp) and 75.23% (EIS) at a concentration of 2.5% the extract. However, the efficiency decreases slightly with increasing working temperature.
2. The cacao peels extracts contain phenolic and alkaloid compounds as main component, and there is an interaction and chemical bonding between these compounds with the steel surface to form a ferro complex compound.
3. The increasing of inhibition efficiency is due to the increase of charge resistance transfer (Rct) as a result of chemical adsorption in the surface. Addition of the extract inhibit the transfer of electrons from the surface of mild steel into the solution, so that the oxidation process of iron atoms decreases.

4. The inhibitor type is mixed type inhibitors in NaCl 1.5M with dominant cathodic inhibitor, obeys Langmuir isotherm adsorption. Cacao peels extract adsorbed on the surface of the mild steel chemical adsorption, with forming a passive layer on its surface.
5. 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 by coordination covalent bond**.**

Acknowledgments
The first author thanks to Ministry of Education, Republic of Indonesia, for BPPS scholarship grant during her doctoral study, and Hibah Disertasi Doktor no: 398/PL9.1.4/LT/2013.

REFERENCES

[1] Yetri. Y; Emriadi, Novesar Jamarun; Gunawarman, *Asian Journal of Chemistry*, **2015**, 27, (3), 875-881
[2] Gunawarman; Yetri. Y; Emriadi; Novesar Jamarun; Ken-Cho, M. Nakai; M.Niinomi, *Applied Mechanic and Materials*, Trans Tech publications Ltd, **2015**, 776, 193-200.
[3] Gunavathy N; Murugavel S.C, *E-Journal of Chemistry,* **2012**, 9, (1), 487-495.
[4] Al-Sehaibani H; *Mat.-wiss.u. Werkstofftech*, **2000**, 31, 1060-1063.
[5] B P. Raja; M.G. Sethurahman, *Iran J.Chem. Eng*, **2009**, 28, 77-84.
[6] Eddy N. O; Awe F;Ebenso E. E, *Int. J. Electrochem. Sci,* **2010**, 5, 1996-2011.
[7] Okafor; Peter C; Ebenso E. E; Udofot J, *Int. J. Electrochem.Sci*, **2010**, 5, 978-993.
[8] Singh A; Singh V.K; Quraish M.A; *International Journal of Corrosion,* **2010**, 1-10.
[9] Hasan S. K; Edrah S, *J. Ind. Res Tech,* , **2011**, 1 (2), 110-113.
[10] Saratha R; Priya S.V; Thilagavathy P, *E- Journal of Chemistry*, **2009**, 6**(**3), 785-795.
[11] Loto C. A, Loto R.T, and Popoola A.P.I, *Int.J. Electrochem. Sci,* , **2011**, 6, 4900-4914.
[12] Matheswaran P and Ramasamy A. K, *E-Journal of Chemistry*, **2012**, 9(1), 75-78.
[13] Okafor P. C, Ebiekpe V. E, Azike C. F, Egbung G. E, Brisibe E. A, and Ebenso E. E, *International Journal of Corrosion*, **2012**, 2012.
[14] K.P. Vinod Kumar, M.S. Narayanan Pillai and G. Rexin Thusnavis, *Portugaliae Electrochimica Act*, **2010**, 28, 373-383.
[15] E. A. Noor, *Int. J. Electrochem Sci*, **2007**, 2, 996-1017.
[16] Loto C. A, O. O. Joseph, R.T. Loto, A.P.I. Popoola, , *Int. J. Electrochem. Sci*, **2013**, 6, 1396-1414.
[17] M. Shyamala, and P.K. Kasthuri, *International Jurnal of Corrosion*, **2012**, 1-13.
[18] M. H. Hussin and M. J. Kassim, Electrochemical, *Int. J. Electrochem. Sci*, **2011**, 6, 1396-1414.
[19] Loto C.A, *J. Mater. Environ.Sci*, **2012**, l(3), 195 – 205.
[20] ASTM Standard G 59-78, *Standard Practice for Conducting PotentiodynamicPolarization Resistance Measurements*, American Society for Testing and Materials, Philadelphia, **1991**, 15-47.
[21] N. Azzeeri, F. Mancia and A.Tamba, *Corrosion Science,* **1982**, 22(7), 675-687.
[22] U.S. Mohanty and K.L Lin, *J. Electrochemical Society,* **2006**, 153, 319-324.
[23]P.A. Schweitzer, *Fundamental of Corrosion Mechanisms, Cause, and PreventativeMethods,* Boca Raton, CRC Press, America, **2010**, 23-24.
[24] Abdallah M, *Portugaliae Electrochimica Acta*, **2004**, 22, 161 – 175.
[25] Sayed, S. Rehim, Abdel, Hazzazi, Omar A, Amin, Mohammed A, and Kpped F, *Journal Corrosion Science,* **2008**, 50, 2258-2271.
[26] Rivera-Grau, L.M. , M. Casales, I. Regla, D.M. Ortega-Toledo, J.A. Ascencio-Gutierrez, J. Porcayo-Calderon, L. Martinez-Gomez, *Int. J. Electrochem. Sci.,* **2013**, 8, 2491 – 2503.