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THEOBROMA CACAO EXTRACT PEELS (TCPE) GREEN INHIBITOR TO RECOVERY THE MECHANICAL PROPERTIES OF MILD STEEL AFTER CORROSION

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ABSTRACT

The high content of secondary metabolites in the cacao peels extracts, has the potential to be used as a corrosion inhibitor on mild steel. Effect of polar extract of cacao (*Theobroma cacao*) peels to the inhibition of corrosion, adsorption properties and mechanical properties in 1.5M HCl solution have been conducted on mild steel. Methods of weight loss, potensiodinamic dan impedance to determine the corrosion rate and efficiency of inhibition, as well as tensile and hardness testing for mechanical properties was conducted with the concentration of extract (0.5-2.5) % by an interval of 0.5%. The surface morphology of samples was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Energy dispersive X-ray spectroscopy (EDX) was used to examine the chemical composition of the surface. Corrosion rate is reduced and efficiency is increased with the increase in the concentration of the extract. The increase in the concentration of the extract is followed by an increase in mechanical properties, namely hardness, strength and fatigue strength. Chemical adsorption is characterized by an increased in the degree of surface of coverage with the rising levels of carbon in the surface of the mild steel with increasing concentrations of the extract. Adsorption isotherms are in accordance with the Langmuir adsorption. The presence of adsorption on the surface of the data is reinforced by EDX, X-ray photon spectroscopy) XPS and X-ray diffraction (XRD) AFM for topography. The addition of polar extract of cacao peels into HCl 1.5M solution is very effective to reduce the attack of corrosion on the surface of mild steel and it can retain mechanical properties of the mild steel after the corrosion.

Keywords: hardness, strength, fatigue, XPS, AFM.

INTRODUCTION

Metals and alloys are widely used in many fields, although the material is easily corroded. Steel is one kind of metal including the category. Corrosion is the degradation of surface quality of a material that the process is slow. Events corrosion can occur anywhere, which can cause damage and loss, either economically or security. Corrosion cannot be avoided almost all the material when interacting with the environment is slowly but surely, will be degraded material quality (Jones, 1996). Steel corrosion, will decline the quality due to the chemical or electrochemical reaction between the steel and its environment. The electrochemical reactions take place in a neutral environment through the following stages:

At the anode: $Fe \longrightarrow Fe^{2+} + 2e$
(oxidation)

At the cathode: $H_2O + ½ O_2 + 2e \longrightarrow 2OH^-$
(reduction reaction)

Total reaction: $Fe + ½ O_2 + H_2O \longrightarrow Fe^{2+} + 2OHFe^{2+} + 4OH^- \longrightarrow 2Fe(OH)_2 \longrightarrow 2Fe(OH) + ½O_2 \longrightarrow 2FeO(OH)\,H_2O \longrightarrow 2H_2O + Fe_3O_4$
(corrosion product)

Many methods is done to slow the rate of corrosion such as electroplating, galvanizing and inhibitor (Umoru *et al.*, 2006). Inhibitor is one way to minimize the effect of material degradation that is often used. Inhibitor serves to slow the rate of corrosion that works by forming a protective layer on the metal surface (Yetri Y *et al.*, 2015a). Inhibitor usually added slightly in acidic environments, cooling water, steam, or other environments.

Until now, the inhibitor is the best solution to protect the corrosion of the metal. Inhibitor is a method of protection that is flexible, being able to provide protection of the environment is less aggressive to the environment the level of corrosion is very high, easy to apply and the effectiveness of the cost is highest because the layer is formed very thin, so small amounts are able to provide broad protection (Terms and Zahrani, 2006).Now, many developed various types of inhibitors of both organic and inorganic. This new inhibitor is expected to reduce the corrosion rate of materials, especially carbon steel material. The use of corrosion inhibitors will provide protection against the failure of material due to the declining quality carbon steel is corroded.

Various types of synthetic inhibitor currently used to replace conventional inorganic inhibitors such as, HBTT (Hydroxy-Benzylidene-amino-Thioxo-Thiazolidin), HBTPH (Dihydroxybenzy- lidene methylquinolin trifluoro-Thio-Propano-Hydrazides), BMIC (Alkaloids, ButylMethylimi - dazolium chlori des), $BMIMHSO_4$ (Butyl-methylimidazolium hydrogen sulfate), Calcium Gluconate, PEGME (Polyethylene GlycolMethyl Ether) and others. But in use, the inorganic inhibitor has a weakness, among others: not biodegradable, toxic and harmful to the environment (Ekanem *et al.,* 2010).

Under these conditions, today people are switching to using organic inhibitors are derived from natural materials. Organic inhibitors are non-toxic, biodegradable and environmentally friendly (Sastri, 2011). Attempts to get environmentally friendly inhibitors, which have been done such as the use of natural ingredients from plants such as extracts of leaves, bark and seeds (Yuhazri *et al.,* 2011). Results of previous studies show that some extracts of natural materials can be used for the corrosion inhibitor. As oxandra asbeckii plant (Lebrini *et al.,* 2011), musa paradica peel (Gopal Ji *et al.,* 2015), asteriscus graveolens (Znini *et al.,* 2012), spirulina pantesis (Kamal.C, *et al.,* 2012), molasses(Raja B. P *et al.,* 2008), zizyphus spina Christi (*Aisha M et al.,* 2010), sebasnian sesban(*Hussein H et al., 2013)*,chlomolaena odorata L (Obot I.B *et al.,* 2012), Pongamia piñata seed (Singh A *et al.,* 2011), mymecodia pendans (Pradityana. A *et al.,* 2016), and Theobroma cacao peel (Yetri Y *et al.,* 2015b). These natural compounds have proven its ability to act as a corrosion inhibitor for some metals and alloys in several different aggressive media. Cacao peels extract is an inhibitor which is capable of improving the efficiency of inhibition of mild steel up to 96% (Yuli *et al.,* 2015a). A number of inhibitors inhibit corrosion by adsorption to form a thin layer that is not visible with a thickness of several molecules of course, some are due to environmental influences form a precipitate which is visible and protects the metal from attacks that corrodes metal and produce products that form a passive layer, and some are eliminating aggressive constituents. The protective membrane is as the cathode, and metal as the anode. Further anions in the anodic inhibitor react with metal ions in solution and close the part that is anodic, so that the rates of corrosion will decrease.

With the increased number of cacao production in Indonesia reaches one million tons/ year, resulting in the production of cacao peels will also increase. These production increases, holds tremendous promise to make the cacao peels extract as an inhibitor of environmentally friendly, which can retain restore the mechanical properties of steel after corrosion.

MATERIALS AND METHODS

Preparation materials

Equipment and materials used to prepare the study include: the preparation of the extracts of cacao, mild steel, and media corrosive hydrochloric acid (HCl) has been described in previous articles (Yetri Y *et al.,* 2015a). Just to remind, the cacao peels extract as inhibitor obtained by maceration. The concentration of inhibitor that is used with variation 0.0; 0.5; 1.0; 1.5; 2.0 and 2.5%. Mild steel used form of bars, cut with diameter of 12 mm and thickness of 2-3 mm for the specimen corrosion rate determination. Preparation specimen for testing the mechanical properties is using ASTM standards. All of the specimen sanded until smooth and finally washed with acetone. Media corrosive hydrochloric acid was used brand products with a concentration of 1.5 M.

The rate of corrosion testing methods

The method used to determine the rate of corrosion is: weight loss, potentiodynamic and impedance. How it works and the formula used by these three methods has been described in detail in a previous article (Yetri Y 2015a and 2015b).

The surface morphology of steel

In a previous article described that corrosion surface morphology analysis using Stereo Carton Trinoculer Photo Optic and S-3400N Scanning Electron microscop. Analysis of the morphology of the surface aims to see mild steel surfaces, without and with extract of cacao peels in medium corrosive HCl 1.5 M. To determine the composition of the elements contained in the steel surface without and with the inhibitor used Electron Dispersion X-Ray (EDX) EMAX software. To determine the type of absorption elements on the surface is used XPS and XRD and AFM is used to view the topography.

Testing mechanical properties

Tensile test using a Universal Testing Machine type RAT-30p CAP 30tf. The test specimen was prepared in accordance with ASTM E-8. To determine surface hardness of mild steel steel used Rockwell Hardness Tester TH 550 with load 980,7N. Preparation of it sto be tested include cutting and sanding. Load and time pressure is set in accordance with the desired (Gunawarman *et al*, 2015). Fatigue specimen testing using the procedure of ASTM E466-2002.

Adsorption surface

Their adsorption on the surface is one of the parameters to determine the effectiveness of the inhibitor extract form natural product are used. XPS analysis is used to determine what elements adsorbed on the surface. AES-XPS tool ESCA 2000 work based on the existence of high-resolution separation of the binding energy of electrons in the core level emitted by the photoelectric effect would come from the X-ray irradiation. Simply XPS works based photon sources are derived from the X-ray irradiation, which passed on a sample. Electrons are located near the core or inner bark emitted out, and then captured by the analyzer and detected in the form of a binding energy of electrons in the core rate. Bond energy of electrons near the core of the interface/ software is displayed in the form of bonds to the intensity of the energy spectrum. The bond energy eventually interpreted as the presence of certain molecules or atoms.

Xpert Pro for XRD measurements is using PANalytical PW 3040/60. In general, XRD is composed of three main parts, namely the X-ray tube, place the object under study, X-ray detector and X-rays are generated in X-ray tubes that contain cathode heats the filament, thereby generating electrons. The voltage difference causes accelerated electrons to shoot the object. When electrons have a high energy level, will hit the object so that the result X-ray.Objek and spin detector capture and record the intensity of light reflection X-ray.

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Detector record and process X-ray signals and processes them in graphical form.

Atomic Force Microscopy (AFM) type nanosurs is a tool for viewing and manipulating atoms nano dimension (size <100 nm). AFM is widely used to investigate the structure, function and adsorption on the surface. These devices are capable of displaying images that are smaller than 20 ms. The microscope also allows displaying images of soft crystals and the polymer surface (A.D.L.Humphris, M.J.Miles, and J.K.Hobbsb, 2005).

RESULTS AND DISCUSSION

The corrosion rate analysis

To remind that further discussions later continuous with the previous article. From the results of corrosion test by the three methods, it appears that the addition of inhibitors, minimize weight loss and slow the rate of corrosion of the corrosion rate before given inhibitor. Conversely increase in inhibitor concentration increase corrosion inhibition efficiency on mild steel surface. This is because, the larger the steel surface in contact with the solution, the more the steel surface coated by a polar extract of cacao peels. The phenomenon is in accordance with protection mechanisms that occur, that poliphenol compounds contained in cacao peels extract has a lone pair of electrons (Yetri Y *et al.,* 2015a) that can serve as electron donors, so it will produce a complex compound with iron. Complex compounds that happen to be stable, not easily oxidized and envelops the metal surfaces of steel, so that the rate of corrosion can be inhibited. (Okafor, P. C. *et al.,* 2012).

Analysis of mechanical properties

The result testing of hardness and tensile for mild steel was shown in Table-1 and 2. Tensile and hardness showed an increase with increasing concentration of the extract. This is supported by the hardness test data, which shows the increase in the concentration of the extract also increases surface hardness mild steel. The increase in the concentration of the extract also increases the resistance of steel against corrosive ions in the corrosive media, so that the rate of corrosion can be inhibited. This means that the higher the concentration of the extract, the amount of extract adsorbed on the surface, so the surface area mild steel covered by peels extract of cacao (Gunawarman *et al.* 2015). The extract adsorbed on the surface of it chemically and formed a thin film coating which is difficult to be vandalized (Leelavathi S and R. Rajalakshmi, 2013).

Table-1. The hardness of mild steel in HCl 1.5M with various concentrations of cacao peels extracts.

Concentration of Extract (%)	Hardness (HRB)
Mild steel (as received)	98.04
0.0	52.85
0.5	56.27
1.0	62.29
1.5	64.47
2.0	67.97
2.5	72.24

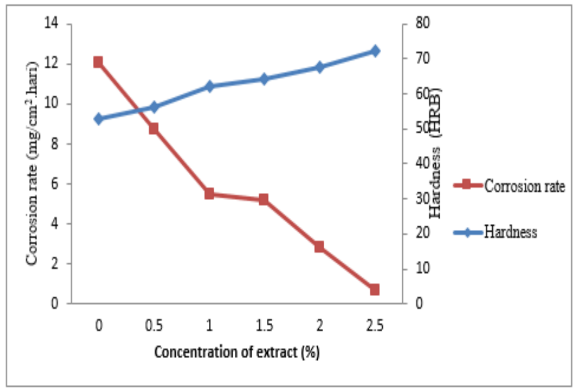

Figure-1. Effect of extract concentration on the rate of corrosion and hardness in HCl 1.5M.

Table-2. The strength of mild steel with various concentrations of the extract in HCl 1.5M.

Concentration of extract (%)	Tensile strength (MPa)	Yeild strength (MPa)
Mild steel (as received)	691.1	445.9
0,0	495.2	340.4
0,5	540.0	360.0
1.0	581.8	371.3
1,5	601.9	462.0
2,0	658.4	512.1
2,5	675.0	550.7

Table-3. Content of the elements identified in EDX testing.

Treatment	Contain of element (% weight)		
	C	Fe	O
Mild steel	0.32	98.79	-
Mild steel + Extract	6.19	92.66	4,33
Mild steel + HCl 1.5M	1.50	29.39	63.54
Mild steel + HCl 1.5M + Extract	16.90	37.43	44.89

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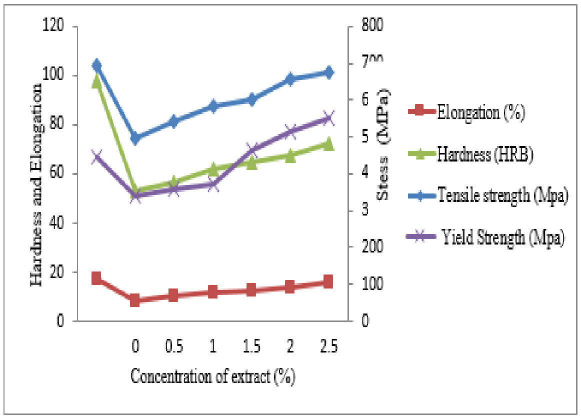

Figure-2. Effect of the extract concentration against ardness, elongation, yield strength, and Tensile in HCl 1.5M.

The amount of extract is adsorbed on the surface illuminated by EDX test results in Table-3. Increased carbon content in the surface of mild steel not only increases the hardness but will also increase the surface of coverage (Afolabi, 2007) the rise the surface of hardness will decrease the rate of corrosion (Gunawarman *et al.*, 2014). For more details, fourth relations mechanical properties can be seen in Figure-2.

Fatigue analysis (Fatigue)

The samples used for testing fatigue are 26 pieces, which were treated with various concentration of the extract in HCl 1.5M can be seen in Table-4.

Table-4. Testing fatigue mild steel with various concentration of the extract in HCl 1.5M.

Sample	Number of Specimens
As received	2
HCl	4
HCl + 0.5 TCPE	4
HCl + 1.0 TCPE	4
HCl + 1.5 TCPE	4
HCl + 2.0 TCPE	4
HCl + 2.5 TCPE	4

Fatigue testing was performed according to ISO 12107, with a statistical estimate of the fatigue strength given in fatigue life. The test conditions are as follows: f = 10 Hz, R = 0.1 (tensile-tensile), Fatigue limit given: 1 x 105 cycles, UTS S35C measured with a tensile strength after being given inhibitor cacao peels extract is 875 MPa. S35C fatigue strength after being immersion in a solution of HCl dropped from 675 MPa to 550 MPa. After addition of inhibitor fatigue strength back toward the original force as can be seen in Table-5 and Figure-3. That is, the fatigue strength increases with increasing concentration of inhibitor added. This occurs due to the adsorption of the cacao peels extracts on steel surfaces. From a series of mechanical properties has been carried out on the steel, shows there have been improvements of mechanical properties after the addition of inhibitor extract of cacao peels.

Table-5. Fatigue strength and fatigue life of mild steel with various concentrations of the extract in HCl 1.5M.

Sample	Maximum cyclic stress (MPa)	Fatigue Life (cycles)
As-received	700	86812
HCl-1	550	31403
HCl-2	600	51131
HCl+0.5TCPE-1	650	28843
HCl+0.5TCPE-2	700	19247
HCl+2.5TCPE-1	700	71185
HCl+2.5TCPE-2	700	16091

XPS analysis

Testing XPS aims to see the film formed, for their adsorption on the steel surface as shown in Figure-4. The spectrum that appears in Figure-4a shows that the coating film on the surface contains elements Fe, O, and C. From Figure-4b detected bond of carbon (C , CC, C = C) that appears at the top of 284.5 ev. Carbon-oxygen single bonds (-CO) on 285,7ev also a carbon-oxygen double bond (-C = O) on 288.4ev, and a combination of single and double bonds (OC = O) on 289,3ev (Satapathy *et al.*, 2009). This data is supported by the analysis of FT-IR spectrum at a wavelength of 1019 cm-1, 1162 cm-1, 1435-1459 cm-1 and 1617-1654 cm-1. The combination is assumed to be a complex compound peels extract of cacao with oxygen in the form of $TCPE_2O_3$, TCPE $(OH)_3$ and TCPE-O-C product. But the spectrum of the signal representing O1s appear on 529,8ev oxide and oxygen of the hydroxyl group at 531,4ev and 533,0ev as in Figure-4c (Satapathy *et al*, 2009).Hydroxyl groups which appears in XPS analysis suitable with the results of FT-IR analysis at a wavelength of 3376-3422 cm-1. Figure-4d shows the peak that appears consists of a mixture of iron corrosion products such as Fe3O4, Fe2O3, FeO, $FeCO_3$ and FeOOH. The peak appeared at 710 and 724ev (Chauhan *et al.*, 2007), (Dang Nam *et al.*, 2014). The results of oxides analysis from XPS reinforced by FT-IR for mild steel oxide at a wavelength of 668 cm^{-1}.

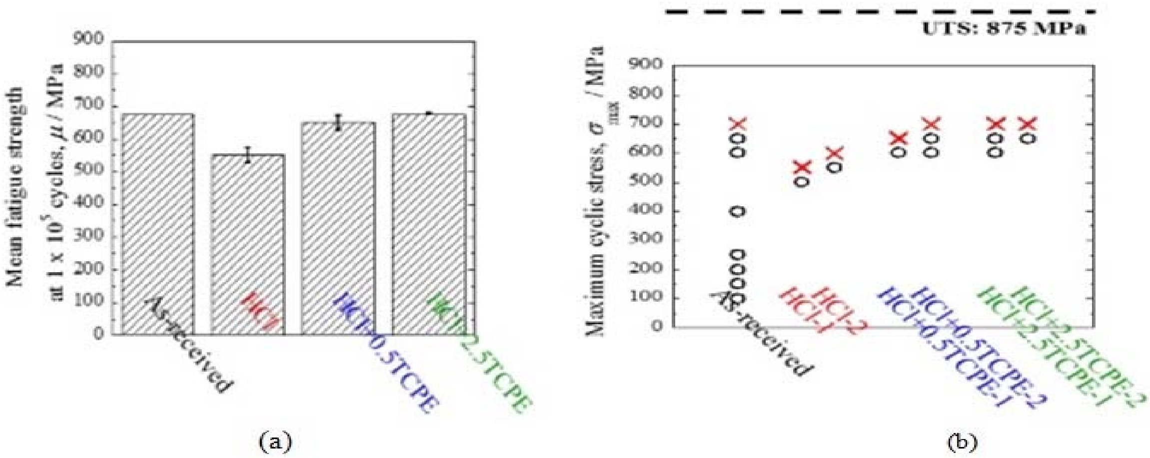

Figure-3. a. S-N curve mild steel, b. Fatigue strength without and with cacao peels extract in 1.5M HCl.

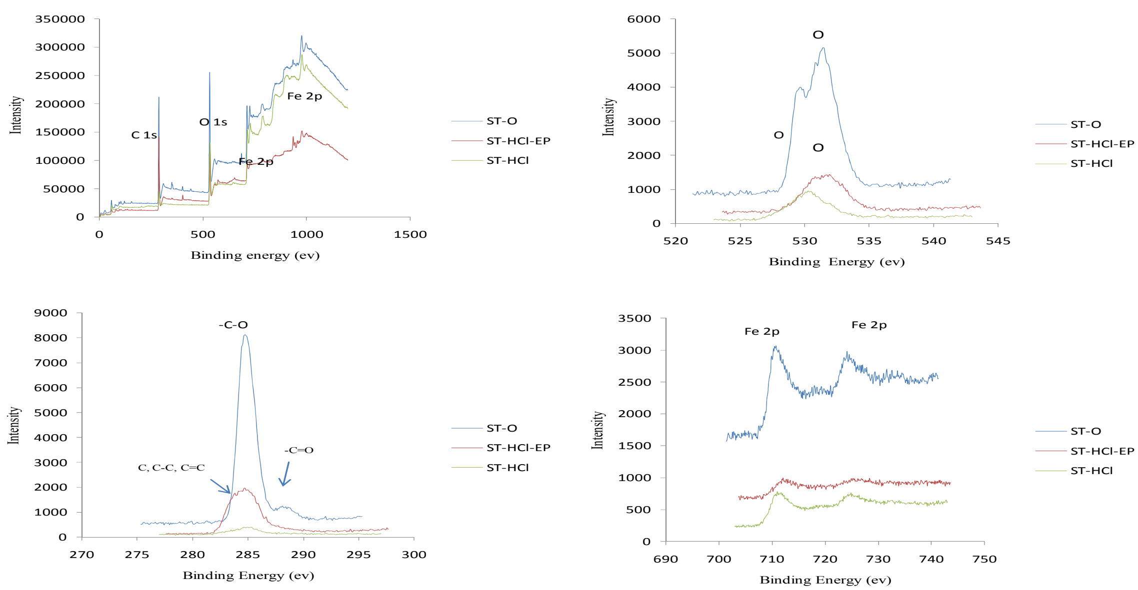

Figure-4. XPS spectrum of: (a). Samples were analyzed, (b). Inhibits oxygen and are not inhibits, (c). Carbon adsorbed, and (d). Fe which appears on the surface of mild steel.

XRD analysis

The result of XRD analysis in Figure-5 conducted on three variables, namely steel, immersed in HCl without and with the addition of the cacao peels extracts. The third of the sample spectrum in Figure-5, only shows the peak of Fe, wherein the spectrum does not show a significant difference. These results indicate that the coating film that forms on the surface of an oxide of iron (Takahashi *et al.,* 2005).From the resulting compounds known that three of these compounds is a common corrosion product on mild steel, namely: FeO, Fe_2O_3 and Fe_3O_4. This data is supported by the results of the analysis of SEM, EDX and XPS earlier, which shows three dominant elements on the surface are: Fe, O, and C. The corrosion products can cause damage to the mild steel surface in the form of localized corrosion or uniform corrosion (Rahim *et al.,* 2012).

Topography analysis

Results of analysis of surface topography using Atomic Force Microscopy (AFM) ParkNX10 clearly shows that there has been a adsorption on the steel surface. Figure-6a shows the mild steel surface as it is after polished with sandpaper, but it looks uneven surface smoothness. Figure-6b shows the mild steel surface after immersed in cacao peels extracts. Its figure is visible adsorption occurs on the surface of steel, where the surface is coated by its extracts in the form of a thin layer of smooth and flat. Figure-6c shows the mild steel surface after immersed into a solution of HCl 1.5M.

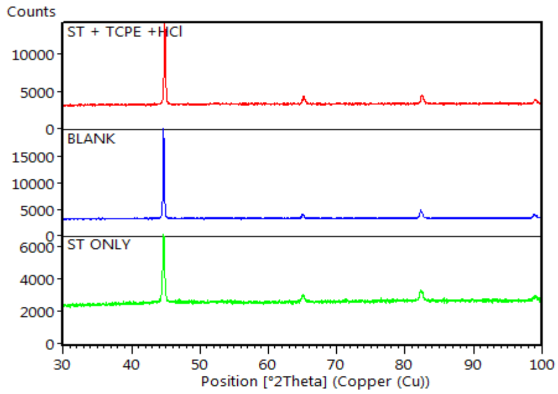

Figure-5. XRD spectrum of the samples by a oxide at each peak: (a). mild steel, (b). mild steel immersed in HCl, (c). mild steel immersed in HCl in the presence of cacao peels extracts.

In the picture looks uneven surface, because it was damaged by corrosive solution. Damage is visible on the surface in Figure-6 is minimized by the addition of cacao peels extracts into HCl 1.5M solution. The results of it can be seen in Figure-6d. The holes former damage by corrosive media is covered by cacaopeels extracts are adsorbed on the surface of the mild steel. By adsorption that occurs on the surface of the mild steel, the corrosion rate can be reduced and the damage caused by corrosion can also be reduced.

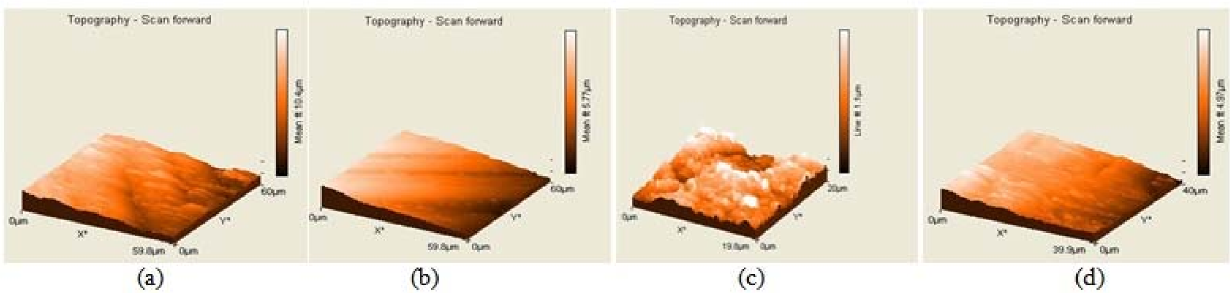

Figure-6. a. Only mild steel, b. Mild steel + Extract, c. Mild steel + HCl, d. Mild steel + HCl + Extract.

Corrosion inhibition mechanism

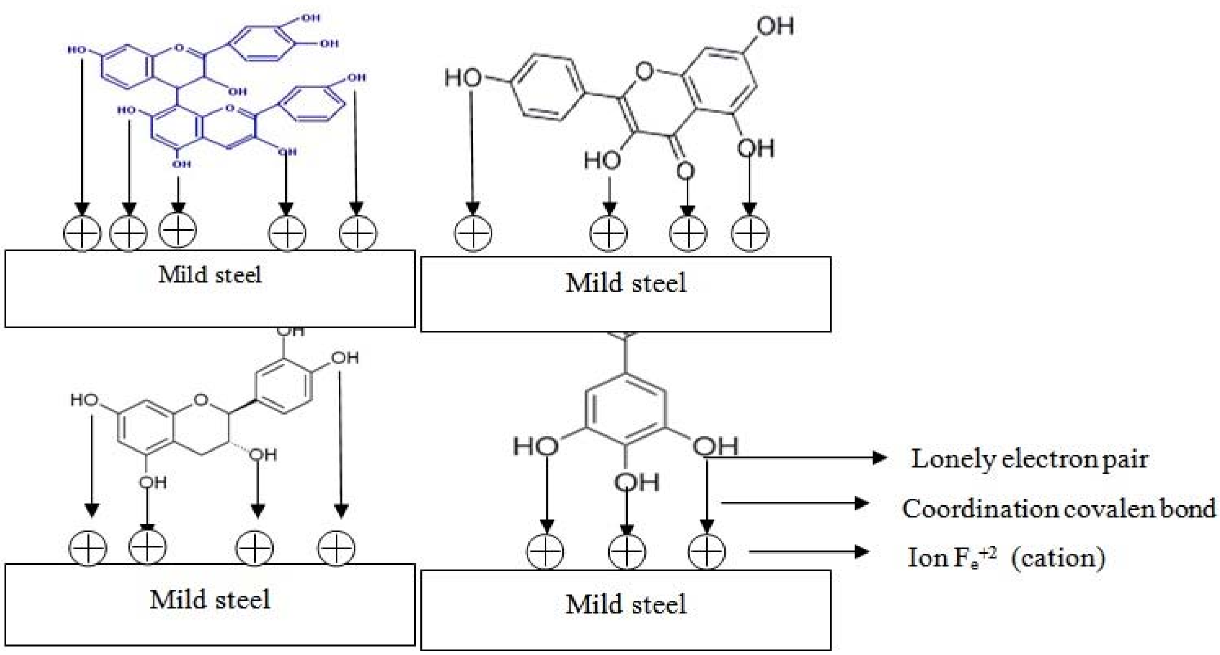

Figure-7. The adsorption process cacao peels extracts compound on the surface of mild steel.

The inhibitor molecule found on the mild steel surface occurs because of the adsorption. Adsorption occurs because the adhesion force between the inhibitor with mild steel surface. Adsorption inhibitor molecules on the surface of mild steel to produce a thin layer (film), which can inhibit corrosion rate. In this case, the extract inhibitor of cacao peels act as forming a thin layer on the surface that can serve as a control of the rate of corrosion to make a separation between the steel with corrosion media (Gerengi *et al,* 2011). The adsorption process cacao peels extract on mild steel surface occurs in functional groups (Leelavathi *et al,* 2013).

The mechanism of inhibition that occurs on the surface of the steel can be explained by the adsorption process and the structure of the components contained in the extract. Inhibition occurs because the adsorption of phytochemical components contained in the extract through an oxygen atom and/ or nitrogen atoms on a metal surface (Leelavathi *et al,* 2013). The complex is adsorbed onto the surface of the mild steel by van der Waals force to form a protective layer, to prevent the mild steel from corrosion (Xiang-Hong Li *et al,* 2010). Some of the major components of the extract of cacao peels are catechin, campferol, gallic acid, and prosianidin shown in Figure-5 (YetriY *et al,* 2015b). All of these compounds that have groups hetero atoms that can donate an electron to form a complex compound on the surface of the mild steel. But effective inhibitor performance also depends on the size of phytochemical constituents of the extract to interact with the metal surface to slow the rate of corrosion (Leelavathi, 2013, Ostovari, 2009).

CONCLUSIONS

The increase of the concentration of peels extract cacao will increase the efficiency of inhibition and surface coverage that occurs on the surface of mild steel. The extent of the surface coverage is strongly influenced by surface adsorption occurs on the surface. Adsorption is formed due to the interaction between the donor atoms of the extract with a mild steel surface. Adsorption occurs following the adsorption isotherm Langmuir. These adsorption raising the carbon content in the surface, improve the mechanical properties of hardness and strength of mild steel. Polar extract of cacao peels able to improve the mechanical properties of the mild steel that is already attacked by corrosion.

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