Corrosion Inhibitor of Mild Steel by Polar Extract of *Theobroma cacao* Peels in Hydrochloric Acid Solution

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In order to decrease corrosion attack of hydrochloric acid on mild steel, *Theobroma cacao* peels polar extract was added as a corrosion inhibitor. Corrosion behavior of the metal was investigated using static accelerated corrosion tests including weight loss method and electrochemical polarization. A mild steel containing 0.3 % carbon is exposed in 1.5 M HCl solution with 0 to 2.5 % of the *Theobroma cacao* polar extract for 48 to 768 h at room temperature (298 K). The solution was also heated 303 to 323 K for 192 h to obtain inhibition efficiency under higher working temperatures. Morphology of sample surfaces was examined by scanning electron microscope. While, the adsorbed film on mild steel surface was measured by Fourier transform infrared spectroscopy. The corrosion test results showed that the inhibition efficiency increases significantly up to 96 % with increasing of *Theobroma cacao* polar extract content. However, the inhibition efficiency decreases slightly with the increase of temperature. The inhibition mechanism of *Theobroma cacao* polar extract on the mild steel surface is mainly chemical adsorption where *Theobroma cacao* polar extract donates a pair of electrons to make a coordination covalent bond with Fe^{2+} ions and then results organometallic compound on the mild steel surface. Surface condition is then improved due to the adsorption, for forming the corrosion protection. The addition of *Theobroma cacao* polar extract into HCl is very effective to reduce corrosion attack on the mild steel.

Keywords: Corrosion, Inhibitor, *Theobroma cacao* polar extract, Mild steel, Electrochemical polarization.

INTRODUCTION

Mild steel is, up to now, widely used in industries due to the availability, fabrication ability, low cost and high tensile strength. However, it is easy to suffer corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, descaling, storage of acids and other chemical processes[1-4]. Therefore, the way of preventing corrosion is very important for mild steel to improve its lifetime and saving maintainance cost as well.

There are several methods of corrosion control and prevention but this work focused on the corrosion inhibitor as an effective way to control corrosion when the metal is exposed in a fluid environment. The performance of a corrosion inhibitor depends on quality of the fluid, chemical composition and flow regime. The common mechanism for inhibiting corrosion involves formation of a coating, passivation which prevents direct access of the substance to the metal. Inhibitors are commonly added to systems such as cooling media, chemical unit, oil and gas production unit, boilers and refinery unit[5].

Corrosion on steel surface as a result of its contact with acids can be minimized to a great extent by the use of inorganic inhibitors, like chromates, phosphates, molybdates, *etc*. The existing inorganic inhibitor compounds have good anticorrosive ability, but most of them are toxic to human and environment. Some of them are not easily biodegradable and their disposal creates pollution problems. Certain plant extracts which are organic compound containing heteroatom like nitrogen, sulphur and oxygen was being investigated as corrosion inhibitors[1-6]. The examples are numerous such as pineapple leaves[6], cacao leaves[7], *Murraya koeniggi* leaves[8], *Azadirachta indica*[9], *Adothoda vasica*[10], *Uncaria gambir*[11], henna[12], vallarai[13], kalmegh[14], UAE neem[15], *Garcinia mangostana*[16], *Sida acuta* leaves[17], argan hulls[18], *Policourea guianensis*[19] and chitin chitosan[20]. Some of them are now commercially use as a substitute of the chemical inhibitors because their environmental friendly, readily available, biodegradable, non-toxic, availability, potentially low cost and ecologically acceptable which make them to be green corrosion inhibitors. Some of these natural substances proved their ability

to act as corrosion inhibitors for many type of metal and alloys in different aggressive media.

There are many other natural substances of tropical plants that potential to be use as a corrosion inhibitor because they contain high amount of tannins ($C_{76}H_{52}O_{46}$), cathechine ($C_{15}H_{14}O_6$) and other inhibitor substances. One of them is *Theobroma cacao* peels that is provided largely in mainlands of Indonesia especially in West Sumatera region. Such kind of peels are usually buried or simply disposed around the cacao plants just after separating from cacao beans. It is, therefore, necessary to find other application that has a higher economic value. This study is to know the potensial use of the peel as a corrosion inhibitor. Addition effect of the peel extracts on the corrosion of mild steel in 1.5 M HCl solution are then investigated using static accelerated corrosion tests.

EXPERIMENTAL

Materials preparation: Mild steel used in this study is commercial steel applied for general construction. The chemical composition of the steel sample was measured by using a Foundry-Master Xpert Spectrometer. The content of each element in weight percentage is Fe (97,8), Mn (0.9), P (0.07), C (0.32), Si (0.22), S (0.06), Cr (0.1), Cu (0.3), Mo (0,02), Al (0.006), Co (0.0053, Ni (0.08). Some specimens with each of weight around 12-15 g were mechanically cut, grinded, polished and then washed with ethanol to remove grease, oxides, *etc*. The specimens were then dried in acetone and preserved in desiccators to prevent reaction with the environment or the formation of oxidation layer which might influences the results of the experiment.

Solutions preparation: The electrolyte solution of hydrocloric acid was prepared by dilution of analytical grade of 37 % HCl with aquades. The concentration of HCl used was 1.5 M. All reagents used in this study were analytical grade.

***Theobroma cacao* polar extract (TCPE):** Two kilograms of fresh samples of *Theobroma cacao* peels were directly collected from a cacao farm in Pariaman region, West Sumatera Prefecture, Indonesia. They then washed carefully with aquades to remove any foreign particles from the peels. The peels were statically pressed and then dried to remove water up to the peel weight downs to 1.10 kg. The dried *Theobroma cacao* peels were then ball milled to obtain *Theobroma cacao* peel powder. The powder was then sifted with wire mesh to obtain fine powders. The fine powders were completely soaked in methanol solution for 96 h, then stirred properly to have homogenous solution and finally filtered again. The filtrate was subjected to evaporation process to remove the methanol in the filtrate. The inhibitor was therefore obtained in its relatively pure form. Subsequently, the filtrate was fractionated by hexane and followed by ethyl acetate to obtain the final product, *i.e.*, polar extract from *Theobroma cacao* peels. The obtained polar extract were then used in preparing various concentrations of solutions by dissolving 0.5, 1, 1.5, 2 and 2.5 % of the extract into 1 L of 1.5 M HCl for each.

Weight loss method: Some polished specimens of the mild steel were immersed in 1.5 M HCl without addition of *Theobroma cacao* polar extract for 48 to 768 h to determine weight loss of the base material as the function of exposure time. Before immersion, the weight of each specimens were measured by digital balance. Some other polished specimens were also immersed in 1.5 M HCl with addition 0.5, 1, 1.5, 2 and 2.5 % of *Theobroma cacao* polar extract for 48 to 768 h. All experiments were performed at room temperature (around 298 K) except for study the effect of temperature described below. After exposure for the specified time, the specimens were removed from the test solution, thoroughly washed with acetone and aquades, dried well and then weighed again. The corrosion rate (V) in g/cm² day and percentage of inhibition efficiency (%) for various concentrations of the inhibitor were calculated using eqns. 1 and 2, respectively[16].

$$V = \frac{\Delta w}{A \times t} \tag{1}$$

where, Δw is weight loss in mg, A is area of the specimen in cm² and t is exposure time in hours (h).

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

In order to know effectivenes of the inhibitation of *Theobroma cacao* polar extract under heated HCl solution, the corrosion rate is also measured at 303 to 323 K. The samples of these temperature test were prepared with the same method described above, but they was exposed only for 192 h within the hot solution.

Potentiodynamic polarization study: Potentiodynamic polarization study was done using computer controlled EDAQ Potentiostat 466-Advanced Electrochemical System. A three electrode cell assembly consisting of a mild steel rod of size 1 mm in diameter and 90 mm in length as working electrode (WE). A platinum electrode were used as reference and auxiliary electrodes (RE) and an AgCl electrode as a counter electrode (CE). The test solution of 100 mL HCl was used for electrochemical measurements at room temperature. Before recording the polarization curves, the mild steel rod as a working electrode was immersed in the test solution for 10 min to reach saturation. Polarization curves were obtained from -800 to 800 mV at room temperature. The corrosion current (I_{corr}), corrosion potential (E_{corr}) and anodic (b_a) and cathodic (b_c) Tafel slopes were then determined. The percentage inhibition efficiency in this case was then calculated using eqn. 3[1]

$$IE\ (\%) = \frac{I_{corr} - I^*_{corr}\ (inh)}{I_{corr}} \times 100\ \% \tag{3}$$

where, I_{corr} and I^*_{corr} (inh) are corrosion current density without and with inhibitor, respectively.

Fourier transform infrared (FTIR) spectroscopy: FTIR test was conducted in this study to identify specified bonding type of functional group and chemical compound of *Theobroma cacao* polar extract and corrosion products. The plant extracts generally contain organic compounds and they will be adsorbed on the metal surface during corrosion process. FTIR test, therefore, can then be used to support the fact that the inhibition mechanism of the mild steel in acidic solutions is related to adsorption of the inhibitor molecules on the metal surfaces.

FTIR spectra were recorded in a Nicolet iS10-FTIR spectro-photometer, which extended from 4,000 to 400 cm^{-1}, using the KBr disk technique. The *Theobroma cacao* polar extract was mixed with KBr and put into the disk. The specimen was prepared according to the standard corrosion test specimen procedure. After immersion in 1.5 M HCl with addition of 2.5 % *Theobroma cacao* polar extract at 298 K (25 °C) for 192 h, the specimen was cleaned with instilled water and then dried with a cold air blaster. Finally, the thin adsorption layer formed on steel surface was rubbed with a small amount of KBr powder in an agate mortar inside a dry box.

Scanning electron microscopy: SEM images of mild steel samples were examined by Hitachi S3400N scanning electron microscopy. The fresh and corroded samples were directly used for SEM examination. The corroded samples here were the mild steel that was immersed into 1.5 M HCl without and with 2.5 % of the inhibitor for 192 h at room temperature.

RESULTS AND DISCUSSION

Corrosion rate and inhibition efficiency: The corrosion rate of mild steel as a function of inhibitor concentration of *Theobroma cacao* polar extract after exposuring for 48-768 h to in the 1.5 M HCl is shown in Fig. 1. It can be seen that the corrosion rate decreases significantly with the increase of *Theobroma cacao* polar extract concentration for all expo-suring times. The decrease of corrosion rate is more remarkably in the case of higher exposuring time and lower concentration of *Theobroma cacao* polar extract. The addition of 2.5 % of *Theobroma cacao* polar extract almost reaches the optimum point of inhibitation to minimaze corrosion attack of HCl. This is clearly shown in Fig. 2 in which the inhibitor efficiency is plotted against inhibitor concentrations for the given expo-suring time. The value of inhibition efficiency obtained from the weight loss increases significantly with the increase of the *Theobroma cacao* polar extract concentration. The maximum of inhibition efficiency is around 96 at 2.5 % *Theobroma cacao* polar extract. As comparison, the addition of 2 and 4 % extract of *Adathoda vasica* in 1 M HCl reaches the inhibition efficiency as much as, respectively, 94 and 96 %[10]. While, the addition of *Centella asiatica* (vallarai) extract into the same solution gives much lower inhibition efficiency, that is only, respec-tively, 58 and 64 %[13]. This indicates that *Theobroma cacao*
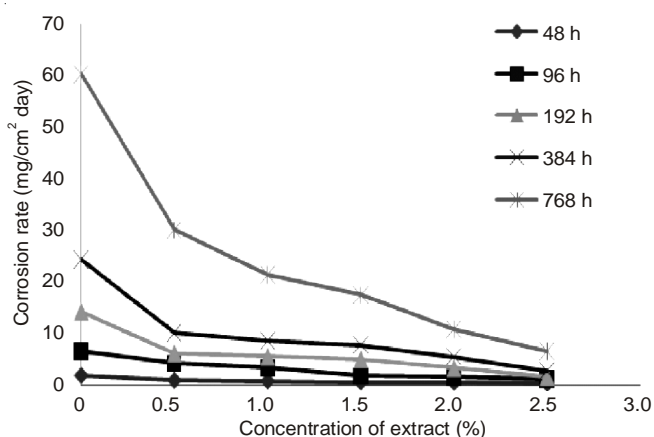

Fig. 1.   Corrosion rate of the mild steel as a function of the concentration of *Theobroma cacao* polar extract for the indicated exposure time
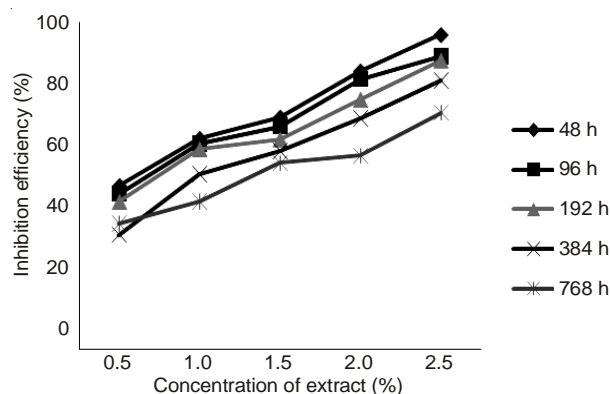

Fig. 2.   Inhibition effeciency (IE) of the mild steel against TCPE concen-tration for the indicated exposure time

polar extract is a relatively good inhibitor for mild steel in hydrochloric acid environment.

Electrochemicals polarization: The potentiodynamic polarization curves for mild steel in 1.5 M HCl without (also called here as blanko) and with addition of the *Theobroma cacao* polar extract are shown in Fig. 3. While, the electro-dynamic parameters of the inhibitor, *i.e.*, corrosion potential E_{corr}, corrosion current density I_{corr}, anodic and cathodic Tafel slopes, b_a and b_c, respectively with and without the presence of inhibitor are listed in Table-1. These results show that I_{corr} values of the acid reduces significantly with the presence of *Theobroma cacao* polar extract. Thus, effectiveness of inhibi-tion also increases remarkably with the increase of the *Theobroma cacao* polar extract content in the acid. This indicates that the inhibition property is due to adsorption of inhibitor molecules on the electrode surface. The shift of E_{corr} value suggest that the inhibitor is mixed type inhibitor and this infers that the inhibitor reduces the hydrogen evolution and anodic disso-lution of mild steel[22,25].

Adsorption isotherm: By assuming the inhibition action of *Theobroma cacao* polar extract is caused by the adsorption of inhibitor on the mild steel surface and obeys Langmuir adsorption isothermal equation[21,22]:

$$\frac{C}{\theta} = \frac{1}{k} = C \qquad (4)$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant and θ is the surface coverage, the plot of C inh/θ *vs.* C is shown in Fig. 4. The phenomenon of interaction between the metal surface and inhibitor can be better under-stood in terms of this adsorption isotherm relationship. A straight line curve indicates that the inhibitor behavior obeys Langmuir adsorption isotherms[21]. The linear correlation coefficient range (R^2) of the present study is obtained in the range of 0.85-0.91. This means that the adsorption of *Theobroma cacao* polar extract on steel surface fairly follows the Langmuir adsorption isotherm at room temperature. This also infers that there is a molecular interaction among the adsorption particles and metal surface and *Theobroma cacao* polar extract is strongly adsorbed on the steel surface as will be proved by SEM micrograph.

Effect of temperature: It is well known that working temperature can modify the interaction between steel electrode

TABLE-1
ELECTROCHEMICAL AND CORROSION PARAMETERS FOR
MILD STEEL WITHOUT (BLANKO) AND WITH ADDITION
OF *Theobroma cacao* PEEL EXTRACT IN 1.5 M HCl

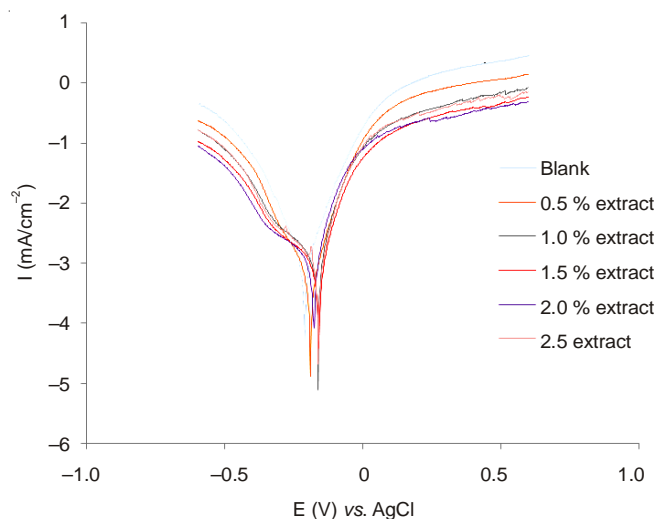| Inhibitor conc. (% in v/v)	I_{corr} (mA cm^{-2})	E_{corr} (Vdec^{-1})	Tafel slope (Vdec^{-1})		Rp Ωm^2	Inhibition efficiency (%)
			b_a	bc		
Blanko	0.0631	-0.2800	2.4000	1.7100	6.8707	-
0.5	0.0159	-0.2750	2.8000	2.3000	34.4754	80.0700
1.0	0.0126	-0.2500	3.6700	2.5700	52.0520	86.6000
1.5	0.0079	-0.2000	2.0000	1.6000	57.3545	88.0200
2.0	0.0066	-0.2200	5.2500	2.6300	115.2546	94.0400
2.5	0.0050	-0.2800	5.7100	2.6700	157.9865	95.6400

Fig. 3. Polarization curves of the mild steel without and with *Theobroma cacao* polar extract in 1.5 M HCl
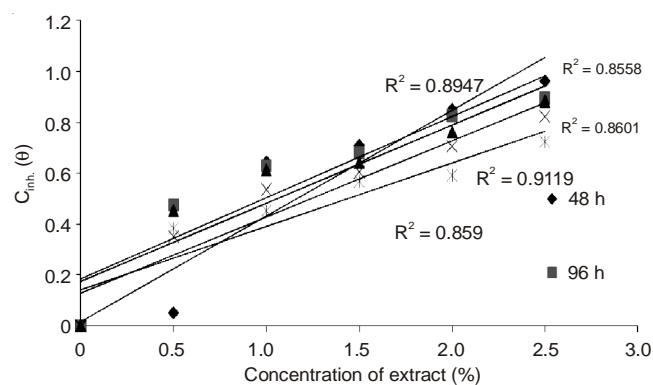

Fig. 4. Langmuir adsorption isotherm trend of *Theobroma cacao* polar extract on the mild steel surface

and acid in the presence and absence of inhibitor[4,18,19]. The effect of temperature on the inhibition efficiency in this case is shown in Fig. 5. The inhibition efficiency keep to increase with increase in concentration of the *Theobroma cacao* polar extract for all investigated temperatures, *i.e.*, 303 to 323 K. However, the inhibition efficiency decreases continuously with the increase of temperature for each given temperature. For example, the inhibition efficiency decreases from around 85 % at 303 K to 60 % at 323 K for 2.5 % *Theobroma cacao* polar extract . The inhibition efficiency decreases with almost same gradient for lower concentration of *Theobroma cacao* polar
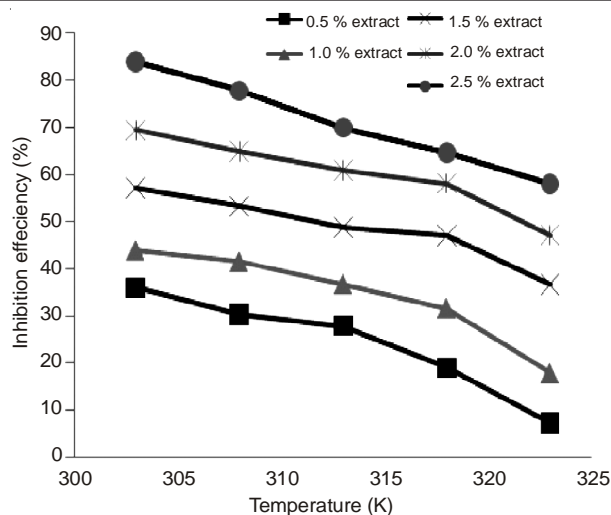

Fig. 5. Effect of temperature on the inhibition efficiency of *Theobroma cacao* polar extract

extract (Fig. 4). The extract has a better function as a inhibitor at higher concentration and at lower temperature. However, the peel extract still have remarkable inhibition efficiency even at low concentration of *Theobroma cacao* polar extract and high temperature. The decrease in the inhibition efficiency of the inhibitor with the increase of temperature might be due to the decrease of adsorption and at same time, desorption of inhibitor is increased. Adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature. As the increase of temperature, the equilibrium between adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant[16,23].

Kinetic and thermodynamic parameters: The Arrhenius plots of log v *vs*. 1/T and log v/T *vs*. 1/T for both uninhibited and inhibited systems are rectilinear with correlation coefficient range level (R^2) around 0.85 for the inhibited ones (Fig. 6). This fair linearity of both curves also confirm that the inhibitor behavior obeys Langmuir adsorption isotherms. The activation energies (E_a) and the heat of adsorption ΔH calculated from the slopes of the curves (Fig. 6ab) are given in Table-2. It can be seen E_a value in this case is relatively higher (> 40 kJ mol^{-1}). This means interaction between Fe and *Theobroma cacao* polar extract in the surface of mild steel is already occured. The type of chemical bonding between the Fe and *Theobroma cacao* polar extract is organometallic complex compound. This bonding is fixed and difficult to be ionized, so that adsorption process is running slowly. The marked changes in E_a suggest that the inhibitor may either participate in the electrode process or may change the potential difference of the metal solution interface by adsorption. Adsorption isotherms provide useful information of the corrosion inhibition mechanism.

Surface morphology: Morphologies of the mild steel surfaces without and with the presence of optimum concentration *Theobroma cacao* polar extract are shown in Fig. 7a-c. It can be seen from Fig. 7a that the mild steel samples before immersion looks very smooth without any corrosion spots. Linear marks in the picture is scratches resulting during polishing process. Fig. 7b shows that the mild steel surface

TABEL-2
SPECTRA FREQUENCIES OF THE *Theobroma cacao*
POLAR EXTRACT AND CORROSION PRODUCT

No	Frequency (cm^{-1})		Functional Group
	Theobroma cacao polar extract	Corrosion Product	
1	1051	1019	C-O (ether)
2	1400	-	C-C=C (asymmetric aromatic)
3	1603	1629	C=O
4	-	2363	H-C-H (phenol)
5	3422	3378	O-H (phenol)
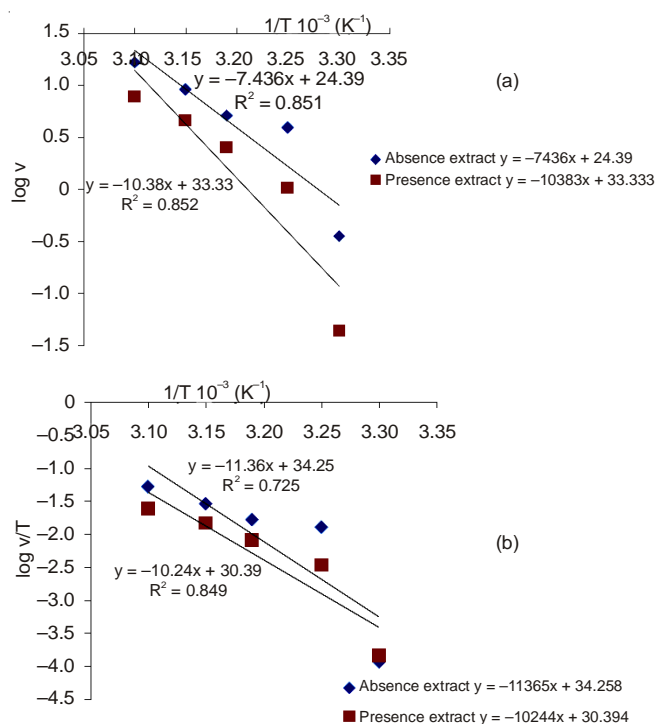
Fig. 6. Arrhenius plots for mild steel immersed in 1.5 M HCl solution in the absence and presence of optimum concentration (2.5 % v/v) of *Theobroma cacao* polar extract (a) log v *vs*. 1/T (b) log v/T *vs*. 1/T

sufferred heavy corrosion damages after immersion in the uninhibited 1.5 M HCl for 192 h. The corrosion products are clearly seen and appeared lepidoteral-like form that shows an aggressive attack of the hydrochloric acid on the steel surfaces. In contrast, the mild steel surfaces has only slight corrosion product with the presence of 2.5 % *Theobroma cacao* polar extract for exposure time of 192 h (Fig. 7c). The corrosion product is identified as adsorbed film on the mild steel surface by FTIR as described below, which do not exist in the case of unhibitted acid (Fig. 7b). This indicates that the film formation efficiently inhibits the corrosion attack into the steel.

Functional group: FTIR spectrum of *Theobroma cacao* polar extract and corrosion product resulting from immersion of the sample in the solution with addition of 2.5 % *Theobroma cacao* polar extract for 192 h are shown in Fig. 8ab, respectively. Fig. 8 shows a significant difference between the two spectra. There are several peaks in Fig. 8a, it is not appear in Fig. 8b, but some new peaks appear in Fig. 8b. Many peaks appear in the same or adjacent frequencies. Identified functional groups of *Theobroma cacao* polar extract (Fig. 8a) is phenol, aromatic rings and ether. Most of these functional groups
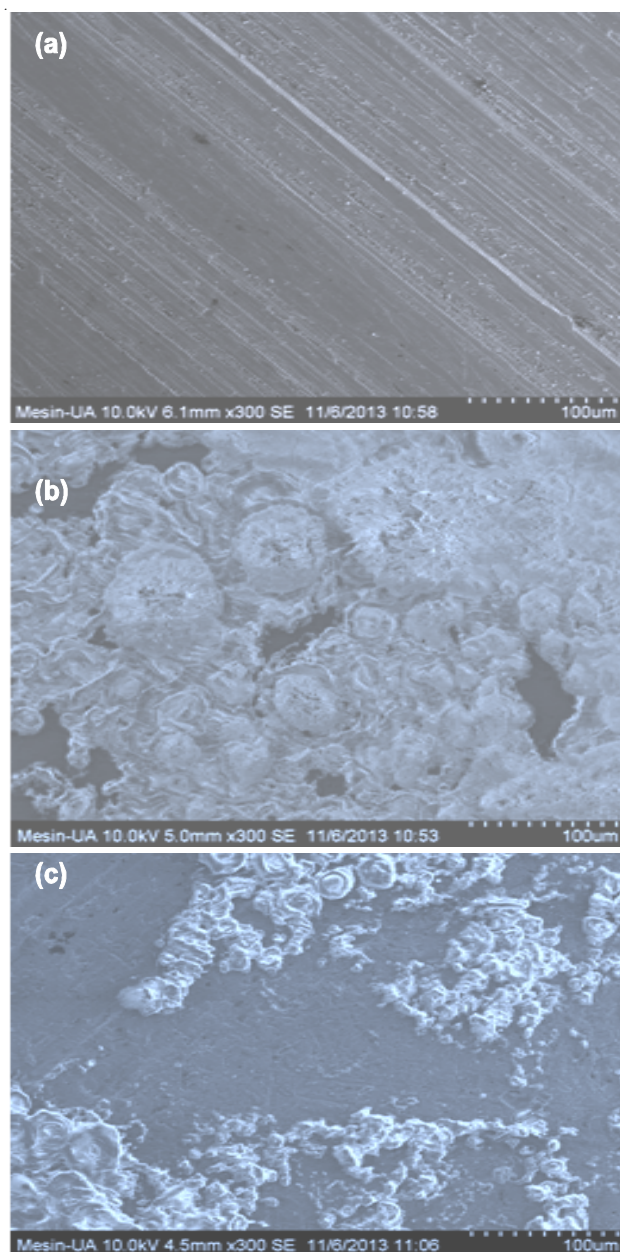

Fig. 7. SEM images of the mild steel (a) before immersion (polished) (b) after 192 h exposuring in 1.5 M HCl without *Theobroma cacao* polar extract and (c) with 2.5 % *Theobroma cacao* polar extract

appear in the corrosion products but with little frequency shifting. For example, functional group of C-O that appear at a frequency of 1051 cm^{-1} is shifted to 1019 cm^{-1}. Functional group of C=O is shifted from 1603 to 1629 cm^{-1}. While the peak of OH is shifted from 3422 to 3378 cm^{-1}. New peak appears at a frequency of 620 cm^{-1} is Fe-H bond. Another new peak at 835 cm^{-1} is suggested due to Fe=O bond stretching. These results clearly confirm that there is an interaction and chemical bonding between metal compounds and extracts the surface area. The identified functional groups from existing peaks in both spectra is shown in Table-2.

Mechanism of inhibition: The results of this investigation clearly indicate that the inhibitive action of *Theobroma cacao* polar extract toward the acid corrosion of steel is attributed to the adsorption of its components of *Theobroma cacao* polar extract onto the steel surface. The important constituents of
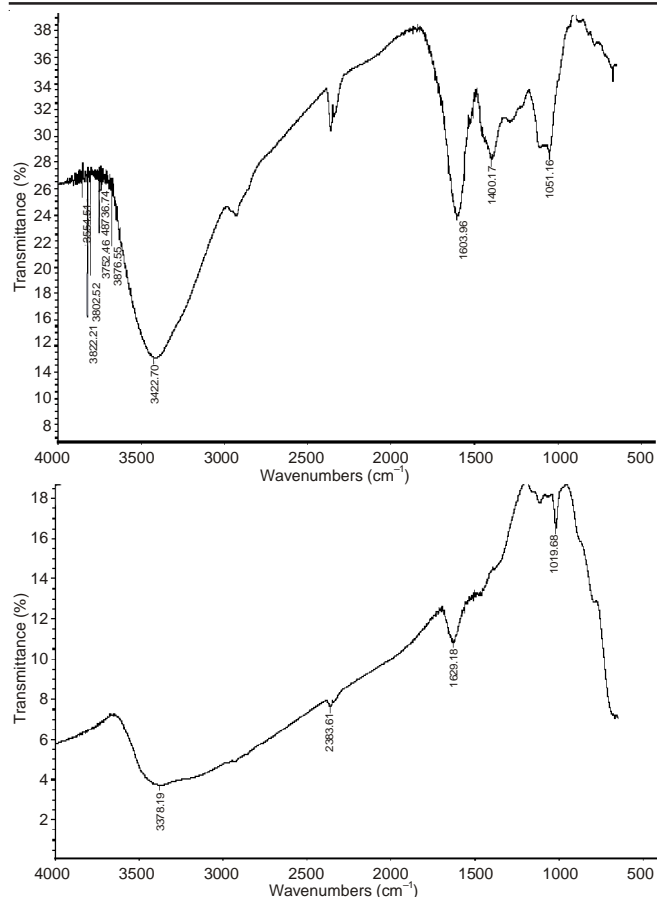
Fig. 8. FTIR spectra of (a) *Theobroma cacao* polar extract (b) adsorption layer formed on the mild steel surface after immersion in 1.5 M HCl with 2.5 % *Theobroma cacao* polar extract for 8 days (196 h)

the polar extract of *Theobroma cacao* peels are confirmed as flavonoids of tannins ($C_{76}H_{52}O_{46}$), instead of cathechine ($C_{15}H_{14}O_6$), epicathechine ($C_{15}H_{14}O_6$), *etc.*[23,27]. *Theobroma cacao* polar extract also contains oxygen atoms in functional groups (O-H, C=C, C-O, C=O) and aromatic ring, which meets the general consideration of typical corrosion inhibitors.

Kinetic and thermodynamical parameters of the corrosion process without and with the presence of *Theobroma cacao* polar extract are shown in Table-3. It can be seeen that value of activation energy (E_a) of the corrosion increases with the addition of the extract. High value of E_a with the presence of *Theobroma cacao* polar extract indicates that corrosion reaction becomes more difficult because it requires a larger energy. Increasing the value of E_a also proves that *Theobroma cacao* polar extract directly influence the chemical reactions that occur on the surface of mild steel. The chemical adsorption occurs by a way of charge transfer or sharing of inhibitors to the surface of mild steel[19]. *Theobroma cacao* polar extract might be protonated in the acid media as follows:
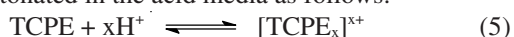
$$TCPE + xH^+ \rightleftharpoons [TCPE_x]^{x+} \tag{5}$$

TABLE-3
KINETIC AND THERMODYNAMIC PARAMETERS OF MILD STEEL IN PRESENCE OF *Theobroma cacao* POLAR EXTRACT IN 1.5 M HCl

No	Indicator	E_a (kJ/mol)	ΔH (kJ/mol)
1.	Blank	142.3782	217.6073
2.	Blank + inhibitor	198.8048	196.1433

The protonated *Theobroma cacao* polar extract may adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. In other words, there may be a synergism between Cl^- and *Theobroma cacao* polar extract, which improves the inhibitive capability of the inhibitor. When protonated *Theobroma cacao* polar extract is adsorbed on metal surface, a coordinate bond may be formed by partial transference of electrons from polar atoms (O atoms) to the metal surface. In addition, owing to lonely pair electrons of O atoms in *Theobroma cacao* polar extract, protonated *Theobroma cacao* polar extract may combine with freshly generated Fe^{2+} ions on steel surface forming metal inhibitor complexes:

$$Fe \rightarrow Fe^{2+} + 2e \tag{6}$$
$$TCPE + Fe^{2+} \rightarrow [TCPE - Fe]^{2+} \tag{7}$$
$$[TCPE_x]^{x+} + Fe^{2+} \rightarrow [TCPE_x - Fe]^{(2+x)+} \tag{8}$$

Such kind of complex compound is adsorbed into steel surface by chemicals bond force. These molecules is chemically bonded with charge transfer to form a protective film and then prevents the mild steel from corrosion. This finding is confirmed by the SEM micrograph (Fig. 7) and FTIR spectrum (Fig. 8). SEM micrographs also show that *Theobroma cacao* polar extract adsorb into steel surface to form a dense and tight protective films.

Mechanisms involved in the inhibition of corrosion of steel can be, therefore, simplified and proposed as follows. *Theobroma cacao* polar extract acts as anion donates a pair of electrons to form a coordination covalent bond with Fe^{2+} ions. The result of this reaction is formation of an organometallic complex compound, which is visible as a thin layer on the steel surface, as shown schematically in Fig. 9.

Conclusions

Corrosion behaviour of 0.3 % carbon mild steel with addition *Theobroma cacao* peel extract (TCPE) in 1.5 M HCl solution was investigated using weight loss method and electrochemical polarization. The corrosion test was conducted under room temperature (298 K) for 48 to 768 h and heated solution (303 to 323 K) for 192 h with 0 to 2.5 % *Theobroma cacao* polar extract addition. Conclusions of this work are as follows:

• Corrosion rate of the mild steel reduces significantly with increasing of *Theobroma cacao* polar extract content and as a consequence, the inhibition efficiency of *Theobroma cacao* polar extract increases significantly with the increase of *Theobroma cacao* polar extract concentration. The inhibition efficiency then slightly decreases with the increase of working temperature. However, the inhibition effciency is still high enough up to working temperature of 323 K.

• *Theobroma cacao* polar extract is adsorbed on the steel surface in accordance with Langmuir isotherm adsorption model which indicates a molecular interaction among the adsorption particles and metal surface. Morever, mixing process of hydrogen evolution and anodic dissolution may occur to during corrosion process.

• The mechanism of inhibition action of *Theobroma cacao* polar extract on the mild steel surface is mainly chemical adsorption where *Theobroma cacao* polar extract donates a
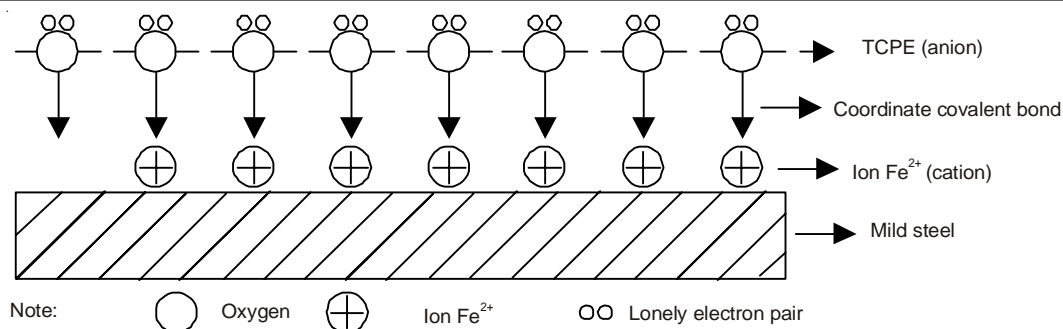
Fig. 9. Schematic diagram of inhibition mechanism of *Theobroma cacao* polar extract on the mild steel surface

pair of electrons to make a coordination covalent bond with Fe^{2+} ions and then results organometallic complex compound on the mild steel surface.

• The addition of *Theobroma cacao* polar extract into solution is very effective to reduce corrosion attack of the hydrochloric acid on the mild steel.

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