RASĀYAN J. Chem.
Vol. 9 | No. 4 |716 - 727 | October - December | 2016
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
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INHIBITORY ACTION OF *Theobroma cacao* PEELS EXTRACT ON CORROSION OF MILD STEEL IN DIFFERENT MEDIA

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ABSTRACT

The inhibitory effect of extract was obtained from maceration of *Theobroma cacao* peels on the corrosion of mild steel in HCl 1.5 M and NaCl 1,5M which was investigated by using weight loss and electrochemical measurement techniques. Morphologies surface of sample and chemical composition as well were observed by a scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX). The results show that the inhibition efficiency increases with increase of *Theobroma cacao* peels extract concentration. The maximum inhibition efficiency in HCl 1.5 M and NaCl 1.5M was found to be 96.26% (weight loss), 92.68% (Tafel), 95.64% (Rp), 85.78% (EIS) and 91.93% (weight loss), 85.90% (Tafel), 90.19% (Rp) and 75.23% (EIS) for a period of 768 h with 2.5%v/v concentration of the inhibitor respectively. Thermodynamic parameters were evaluated from temperature studies. Results were fitted into suitable adsorption isotherms. Electrochemical measurements infer that the extract acted through mixed mode of inhibition. SEM studies confirmed that corrosion protection of mild steel was due to the adsorption of inhibitors. Efforts were made to analyze the effectiveness of peels extract of *Theobroma cacao* peels in industrial processes.

Keywords: *Theobroma cacao* peels, Mild steel, Corrosion inhibition, GC-MS.

INTRODUCTION

Mild steel is the most preferable material in many industries due to its low cost and easy availability. Acids are used in many industries especially for cleaning, pickling and descaling. In order to reduce the corrosive action in aggressive environment, the inhibitory nature of many organic compounds containing hetero atoms like N, S and O which have high basicity and electron density has been studied[1]. Many heterocyclic compounds and natural products were evaluated for their corrosion inhibition such as triazoles[2], quinoline[3] and pyridine[4], lignin and tannin[5], cinchona alkaloids[6] and pomegranate alkaloids[7] have been evaluated as very effective acid corrosion inhibitors in standard as well as in stringent conditions. Inhibition of corrosion was studied with the extracts of, *Ficus benghalensis* bark[8] , *Ananas comosus*[9], *Theobrema cacao* peels[10], *Mangifera indica*[11], *Murraya Koenigii*[12], *Sesbania grandiflora* seeds[13], *Benign Kuchla seed*[14], *Datura metal*[15], *Callistemos* leaves[16], *Mentha pulgeium*[17], *Canna Indica*[18], *Canavalia ensiformi*[19] and, *Piper Nigrum Linn*[20] *etc*. The studied natural inhibitors have been found to be highly eco-friendly and possess no threat to the environment. Hence the present investigation was aimed to evaluate the efficacy of *Theobroma cacao* peels extract against the corrosion of mild steel.

Brief Literature Review

Chemical Composition of *Theobroma cacao* peels extract

In order to identify the individual compounds in *Theobroma cacao* peels extract Gas Chromatograph-Mass Spectrometry (GC-MS) technique was used[21]. The identification of the essential compounds was achieved by comparing obtained mass spectra of unknown peaks with those stored in the NIST (National Institute of Standards and Technology) and Wiley mass spectral electronic libraries. Identifications were confirmed by comparison with authentic substances used as references and by using of linear retention indices (LRI). Relative area values (as a percentage of total volatile composition) were directly obtained from total ion current (TIC). All analyses were carried out in duplicate. The chromatogram of extract is shown in Figure-1 and the chemical compounds identified in the *Theobroma cacao* peels extract are presented in Table-1.

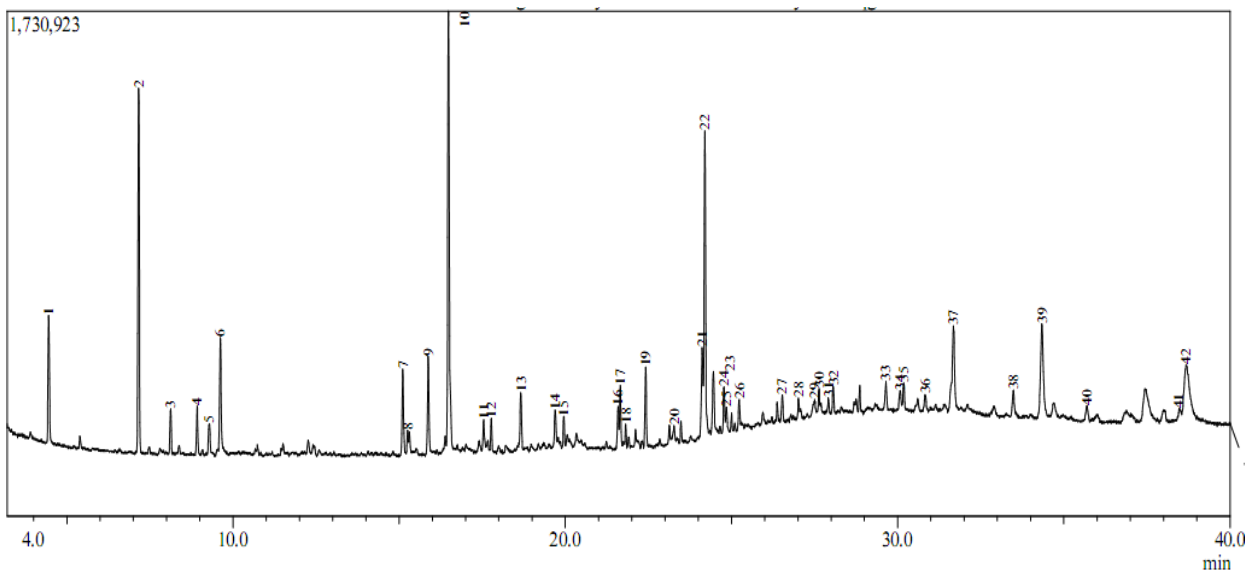


Fig.-1: Total Ion Chromatogram resulting from the *Theobroma cacao* peels extract obtained by maceration

Table-1: The chemical compounds identified in the *Theobroma cacao* peels extract by GC-MS analysis

No	Name of Compound	Formula	Retensi Time (min)
1.	2 pentanon 4 hidroxi-4 methyl	$C_6H_{12}O_2$	4.450
2.	Alpha pinene	$C_{10}H_{16}$	7.158
3.	Beta-pinene	$C_{10}H_{16}$	8.125
4.	Trans-beta-ocimene	$C_{10}H_{16}$	8.917
5.	Beta-terpinyl acetate	$C_{12}H_{20}O_6$	9.292
6.	Benzeenamine	C_7H_9N	9.619
7.	Eugenol	$C_{10}H_{12}O_2$	15.108
8.	2,3,4,4,-tetraprophy-1-(trimethylsilyl)-1,3 diaza-2,4 diborabutane	$C_{18}H_{44}B_2N_2OSi_2$	15.250
9.	Phenol-2 methoxy-4(2-propenyl)	$C_{12}H_{14}O_3$	15.875
10.	Phenol-2 methoxy-4(1-propenyl)	$C_{10}H_{12}O_3$	16.483
11.	Tetra decane	$C_{14}H_{30}$	17.542
12.	Silicate anion tetramer	$C_{24}H_{72}O_{12}Si_{12}$	17.775
13.	Caryophyllene oxide	$C_{15}H_{24}O$	18.658
14.	Patchouli alcohol	$C_{15}H_{26}O$	19.692
15.	Benzoic acid	$C_{16}H_{33}O_4Si_3$	19.950
16.	Undecanone	$C_{13}H_{26}O$	21.583
17.	Neophytadine	$C_{20}H_{38}$	21.650
18.	Silicate anion tetramer	$C_{24}H_{72}O_{12}Si_{12}$	21.817
19.	Hexadecanoic acid	$C_{17}H_{34}O_2$	22.417
20.	Tetracasanol	$C_{26}H_{50}O$	23.275
21.	Oxabicyclo	$C_{12}H_{22}O$	24.117
22.	Octadecanoic acid	$C_{19}H_{36}O_2$	24.200

23.	Heptacosanoic acid	$C_{28}H_{56}O_2$	24.458
24.	Ethyl linoleat	$C_{20}H_{36}O_2$	24.775
25.	Ethyl 9-hexadecanoate	$C_{18}H_{34}O_2$	24.850
26.	Hexadecane	$C_{16}H_{32}$	25.233
27.	5 Hydroxydodecanoic acid lactone	$C_{12}H_{22}O_3$	26.520
28.	Decasanol	$C_{22}H_{46}O$	27.017
29.	2-Octhycyclopropene-1-heptanol	$C_{18}H_{34}O$	27.500
30.	Benzeneacetic acid, alpha,3,4 tris (trismethylsilyl) oxy	$C_{20}H_{40}O_5Si4$	27.630
31.	Docosane	$C_{22}H_{46}$	27.917
32.	1,2 Benzenedicarboxyline	$C_{24}H_{38}O_4$	28.058
33.	Tricosane	$C_{23}H_{48}$	29.650
34.	9-Octadecenamide	$C_{18}H_{35}NO$	30.075
35.	3,4 Dihydroximandelic acid-tetramers	$C_{20}H_{40}O_5Si_4$	30.183
36.	Thiogeraniol	$C_{10}H_{18}S$	30.825
37.	Docosane	$C_{22}H_{46}$	31.675
38.	Silicone polimer	$(C_{14}H_{42}O_5Si_6)n$	33.483
39.	Pentatria contane	$C_{35}H_{72}$	34.342
40.	Benzoic acid 2,6 bis (trimethylsilyl) oxy, trimethyl ester	$C_{16}H_{30}O_4Si_3$	35.70
41.	Benzene acetic acid, alpha 3,4-tris 9 trimethylsilyl) oxy, trimethyl	$C_{20}H_{40}O_5Si_4$	38.462
42.	Ergastone 3,12-diol (3 alpha, 5 beta, 12 alpha)	$C_{28}H_{50}O_2$	38.675

EXPERIMENTAL

Mild steel specimen with the following chemical composition in wt % C, 0.32; Si, 0.22; Mn, 0.9; S, 0.06; P, 0.07; Mo, 0.2; Cr, 0.1 and Fe, 97.8; was used. Mild steel was cut into small coupons with diameter of 25.20 mm and a thickness of 2-3 mm size and used for immersion studies. Coating samples with 1 cm^2 exposed area were used for electrochemical studies. The specimens were duly prepared by mechanical polishing and degreasing methods. They were dried, stored in desiccators and used for all studies. Since HCl and NaCl are widely used in industries, stock of both solution1.5M were prepared and used throughout the experiment. Cacao peels is cleaned of dirty, then chopped into small pieces and dried in the open air without sunlight for 14 days. Skin that has been dried, ground up into a powder. Cacao peels powder 200 grams, put in macerator, then added 70% methanol in 1 L. Then the mixture was stirred and left in a macerator for 4-5 day. Maceration results filtered by using filter paper, 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 extracts ready to be used as inhibitors.

Weight loss measurements were carried out in triplicate for different duration *viz*, (48, 96, 192, 364 and 768 h) and temperature variation was from 303 K to 323 K. From the weight loss values were determined corrosion rate and inhibition efficiency. Electrochemical studies were carried out using conventional three-electrode system, using computer controlled EDAQ Potentiostat 466-Advanced Electrochemical System and Galvanostate AUTOLAB PGSTAT 320N Electrochemical Impedance Spectroscopy were used for data acquisition and analysis. Efforts have been taken to analyze the effectiveness of the peels extract of *Theobroma cacao* industrial processes.

RESULTS AND DISCUSSION

Effect of inhibitor concentration and immersion time

The variation of inhibition efficiency for different extract concentration of *Theobroma cacao* peels is listed in the Figure 2. Maximum inhibition efficiency for HCl 1.5M and NaCl 1.5M was found to be 96.26% and 91.93% with 2.5%v/v concentration of the inhibitor respectively. This behavior may be attributed to the increase of the surface coverage by the extract, which retards the corrosion of mild steel.

From Figure-2, it is noticed that in HCl 1.5M the inhibition efficiency increases with increase of immersion time and concentration of extract from 2.5 %v/v. From the values it can be inferred that as the immersion time increases the protection efficiency increases up to 96.26% at 48 h, thereby indicating the enhanced stability of the adsorbed constituents of the extract on mild steel surface. In NaCl 1.5M the inhibition efficiency increased with increase in concentration and immersion time of the extract to give a protection efficiency of 91.93%. The consistent behavior of *Theobroma cacao* peels extract with an increase in immersion time indicates the stability and persistence of the inhibitor layer on the metal surface[18].

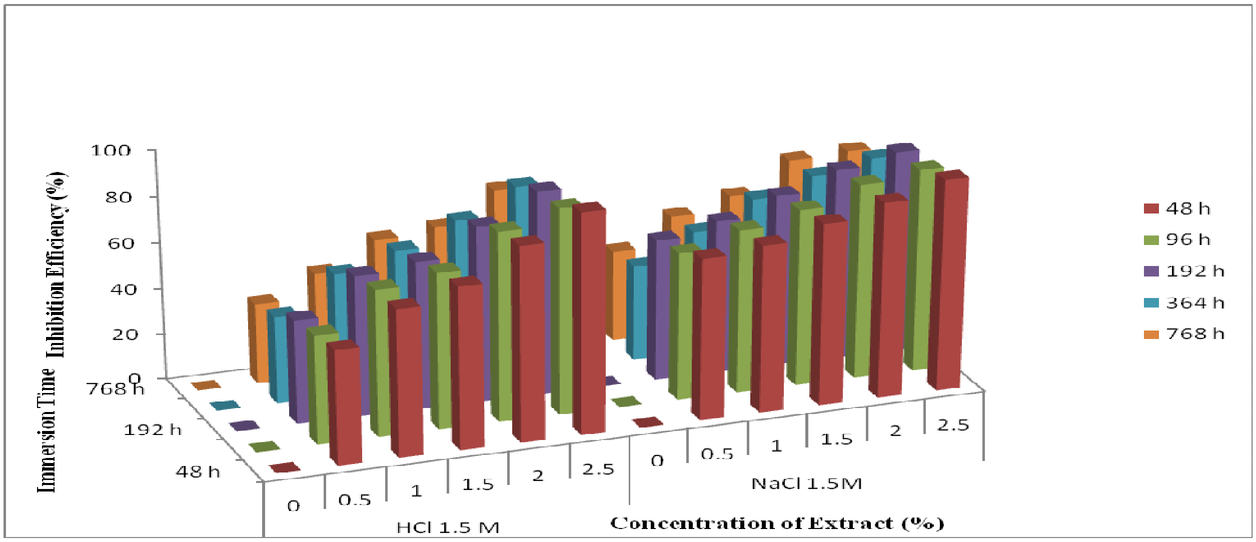


Fig.-2: Inhibition efficiency as a function of immersion time and concentration

Influence of temperature

Temperature can modify the interaction between iron electrode and acid in the presence/ absence of inhibitor. To determine the energy of activation of corrosion and thermodynamic parameters, the weight loss measurements were carried out from 303 K - 323 K in the absence and presence of various concentration of *Theobroma cacao* peels extract. From Figure-3, it was inferred that inhibition efficiency increases with increase of extract concentration at all investigated temperature in both medium. Hot acid solutions are generally used for removing mill scales (oxide scales) from the metal surface in various industries at elevated temperature such as 60 ˚C in HCl.

In the present investigation, the extract functions as a promising inhibitor at higher concentration and at higher temperature. Even at lower concentration of cacao peels extract could also furnish remarkable inhibition efficiency. This can be explained by Tulsi[22], the decrease in the inhibition efficiency of the inhibitor with increase in temperature might be due to adsorption and desorption of inhibitor. Adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature. With 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[23].

Adsorption Isotherm

The phenomenon of interaction between the metal surface and inhibitor can be better understood in terms of adsorption isotherm. A plot of log (θ / (1 - θ)) *vs.* log C and θ *vs.* log C gave a straight line indicating that the inhibitor under the study obeys Langmuir adsorption isotherms respectively[24]. This may also infer that there is a molecular interaction among the adsorption particles and metal surface.

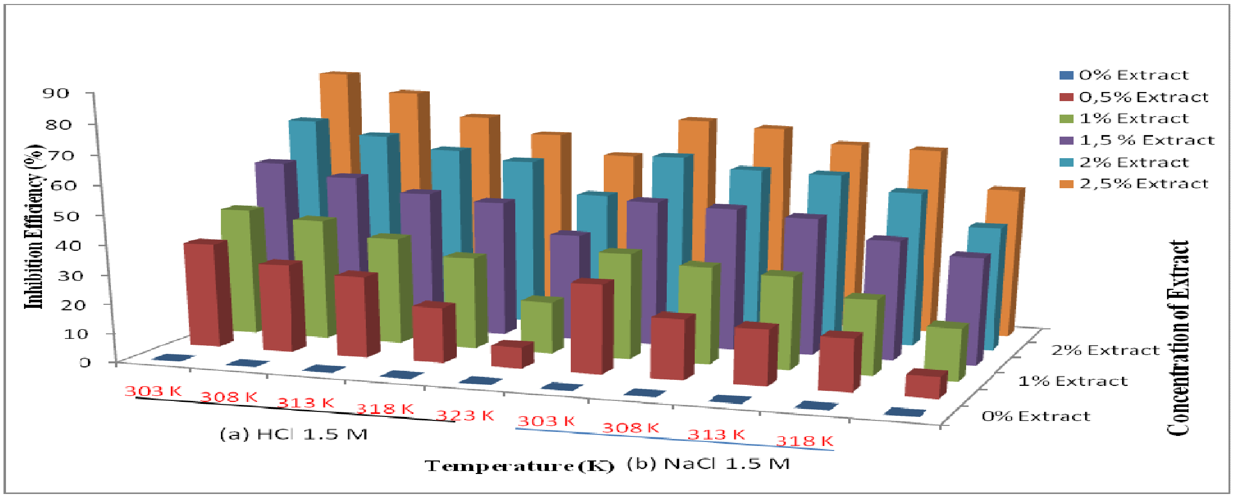


Fig.-3: Effect of temperature on the corrosion of mild steel in (a) HCl 1.5M and (b) NaCl 1.5M in the absence and presence of various inhibitor concentrations.

Kinetic and thermodynamic parameters

The Arrhenius plots of log C.R *vs.* 1/T for both uninhibited and inhibited systems are rectilinear. The activation energies (Ea) calculated from the slopes of the curves given in Table-2. The marked changes in Ea suggest that the inhibitor may either participate in the electrode process or may change the potential difference of the metal solution interface by adsorption.

The values of free energy of adsorption were calculated using the standard equation[25],

$$\log C = \log (\theta / (1 - \theta)) - \log B \quad (1)$$

Where, $\log B = -1.74 - (-\Delta G / 2.303\ RT)$, θ = Surface coverage, C = Concentration, ΔG = Free energy of adsorption, R= Gas Constant, T = Temperature.

The values obtained are presented in Table-2. Results obtained indicate that the values of ΔG are negative in both the cases indicating the spontaneous adsorption of *Theobroma cacao* peels extract and it is strongly adsorbed on the mild steel surface[24]. The increase in ΔG with increasing concentration also indicates the strength of adsorption. The value of ΔG, indicates that the inhibitor function by physically adsorbing on the surface of the mild steel. Generally values of ΔG up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and charged metal (which indicates physisorption) while those are more negative than -40 kJ mol^{-1} involving charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorptions)[25]. Physical adsorption is as a result of electrostatic attraction between charged metal surface and charged species in bulk of the solution. Adsorption of negatively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface[26].

The heat of adsorption ΔH and entropy of adsorption ΔS are calculated from free energy of adsorption by Gibbs Helmholtz equation. The values of ΔH indicate that both physical and chemical adsorption occurred (*i.e.* comprehensive adsorption) in both the system[27]. That is to say, since the adsorption heat approached the general chemical reaction heat, the chemical adsorption might occur accompanied by physical adsorption (electrostatic interaction). The positive ΔS values accompanied with endothermic adsorption process in both acid medium[28].

Electrochemical measurements

Polarization studies

In order to find out the nature of the inhibitor, mode of action, mechanism of reaction, electrochemical techniques such as Tafel, and linear measurements were carried out. Typical potentiodynamic polarizing curve shows the inhibitory action of *Theobroma cacao* peels extract for both acid and alkaline are given in Figure-4. The corrosion parameters such as E_{corr}, I_{corr}, Tafel slope constants (b_a and b_c), linear polarization resistance (R_p) obtained from these curves is presented in Table-3.

Table-2: Kinetic and thermodynamic parameters of mild steel in presence of *Theobroma cacao* peels extract in HCl 1.5M and NaCl 1.5M

Media	No	Indicator	Ea (kJ/mol)	ΔH (kJ/mol)	ΔG° (kHz/mol)	ΔS (kHz/mol)
HCl 1,5 M	1.	Blank	142.38	217.61	-	1.53
	2.	Blank + inhibitor	198.81	196.14	20.61	1.90
NaCl 1,5M	1.	Blank	98.67	96.11	-	0.32
	2.	Blank+ inhibitor	100. 84	98.29	-71.81	0.56

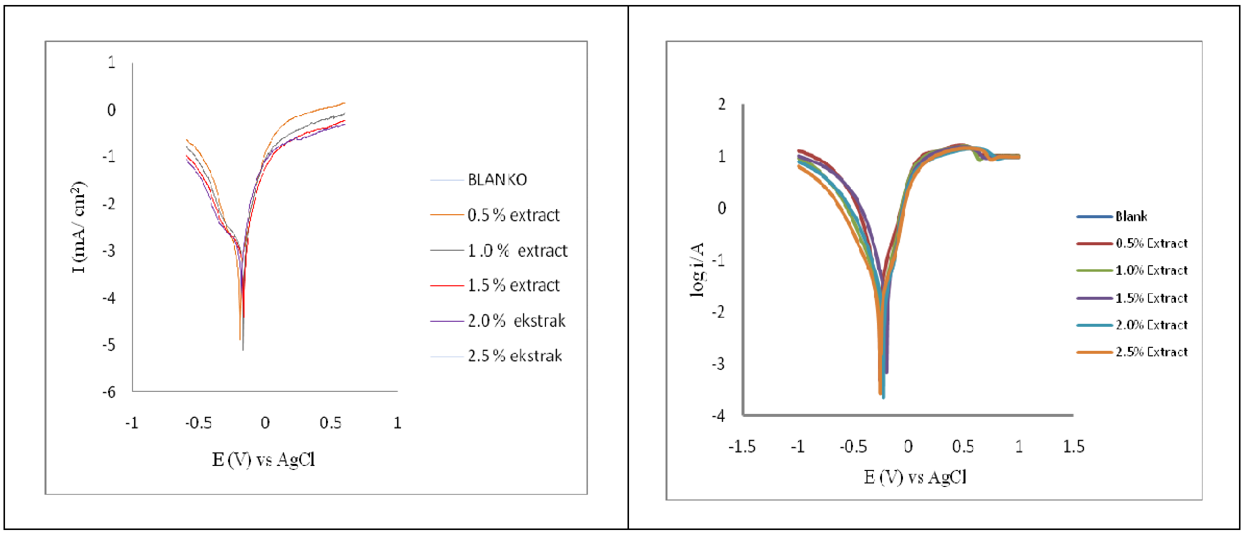


Fig.-4: Polarization curve of mild steel in presence of *Theobroma cacao* peels extract in (a) HCl 1.5M and (b) NaCl 1.5M

I_{corr} was found to decrease as the concentration of the inhibitor increases. This confirms the inhibitory action of *Theobroma cacao* peels extract on metal surface. The E_{corr} value has not been shifted to any particular direction from the blank value, which also 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 in both medium revealed that the inhibition of corrosion of mild steel is under mixed control in both anodic dissolution and cathodic hydrogen evolution mechanism are affected in presence of the inhibitor.

It can be concluded from the results obtained that *Theobroma cacao* peels extract act as a mixed type inhibitor in both media. The increase in resistance polarization values with increase in concentration of inhibitor indicates the effective inhibitory nature of the inhibitor. The inhibition efficiency was calculated by polarization technique was found to increase by increasing the concentration of the extract. Inhibition efficiency was found to be 92.68% and 85.98% in HCl 1.5M and NaCl 1.5M with 2.5%v/v of the extract.

Impedance studies

Impedance parameters such as R_{ct} and C_{dl} obtained are presented in the Table-4. Values of R_{ct} and C_{dl} infer that the inhibition is due to adsorption of inhibitor on mild steel surface. The radius of the semicircle was found to increase in inhibitor concentration (Figure-5). Impedance diagrams show that the corrosion of mild steel is controlling inhibitor (Figure-4) by charge transfer process. Maximum inhibition efficiency using R_{ct} values was found to be 87.78% and 86.53% in HCl 1.5M and NaCl 1.5M respectively at 2.5%v/v concentration. Using C_{dl} values the maximum surface coverage was found to be 0.612 and 0.605 in HCl 1.5M and NaCl 1.5M at 2.5%v/v concentration of extract. The results show that *Theobroma cacao* peels extract is quite effective in retarding dissolution of mild steel in both examined media

Table-3: Electrochemical and corrosion parameters for mild steel in the presence of *Theobroma cacao* peels extract in HCl 1.5M and NaCl 1.5M.

Media corrosive	Inhibitor Conc.(% in v/v)	I_{corr} (mA cm^{-2})	E_{corr} ($Vdec^{-1}$)	Tafel slope ($Vdec^{-1}$)		Rp Ωm^2	IE (%) Icorr	IE (%) Rp
				b_a	bc			
HCl 1,5 M	Blank	0.0631	-0.2800	2.4000	1.7100	6.8707	-	-
	0.5	0.0159	-0.2750	2.8000	2.3000	34.4754	74.8100	80.0700
	1.0	0.0126	-0.2500	3.6700	2.5700	52.0520	80.0300	86.6000
	1.5	0.0079	-0.2000	2.0000	1.6000	57.3545	87.4800	88.0200
	2.0	0.0066	-0.2200	5.2500	2.6300	115.2546	89.5400	94.0400
	2.5	0.0050	-0.2800	5.7100	2.6700	157.9865	92.6800	95.6400
NaCl 1,5 M	Blank	0.0600	-0.2700	1.8000	1.1400	7.2800	-	-
	0.50	0.0500	-0.2800	3.6000	2.8000	13.3300	18.7000	45.3900
	1.00	0.0500	-0.2200	6.0000	3.7500	21.4600	25.8300	66.0700
	1.50	0.0300	-0.2100	5.0000	2.5000	27.6600	29.1700	73.6900
	2.00	0.0200	-0.2100	5.6000	3.2000	39.6700	68.3000	81.6500
	2.50	0.0100	-0.2200	4.7000	2.2500	74.2400	85.9000	90.1900

Industrial application of *Theobroma cacao* peels extract on mild steel

There is a class of chemical inhibitors which work by removing electrons from the metal, thereby pushing the potential into a positive region in which an oxide film spontaneously forms. The result is shown in a stable, passive surface with a very low corrosion rate. Industries apply this technology in processes in which the inhibitor can be conveniently added without causing environmental or health problems.

One of the categories of corrosion inhibitors are those which form a surface layer of a foreign chemical compound provided by the inhibitor itself. Many commercial inhibitors, calgon, for example, is a solution of sodium hexametaphosphate, a condensed phosphate polymer based on the unit $(-PO_3^-)_n$ is used as an inhibitor in potable water systems (drinking water) because it is non-toxic and is widely used in large institutions such as hotels and hospitals[29].

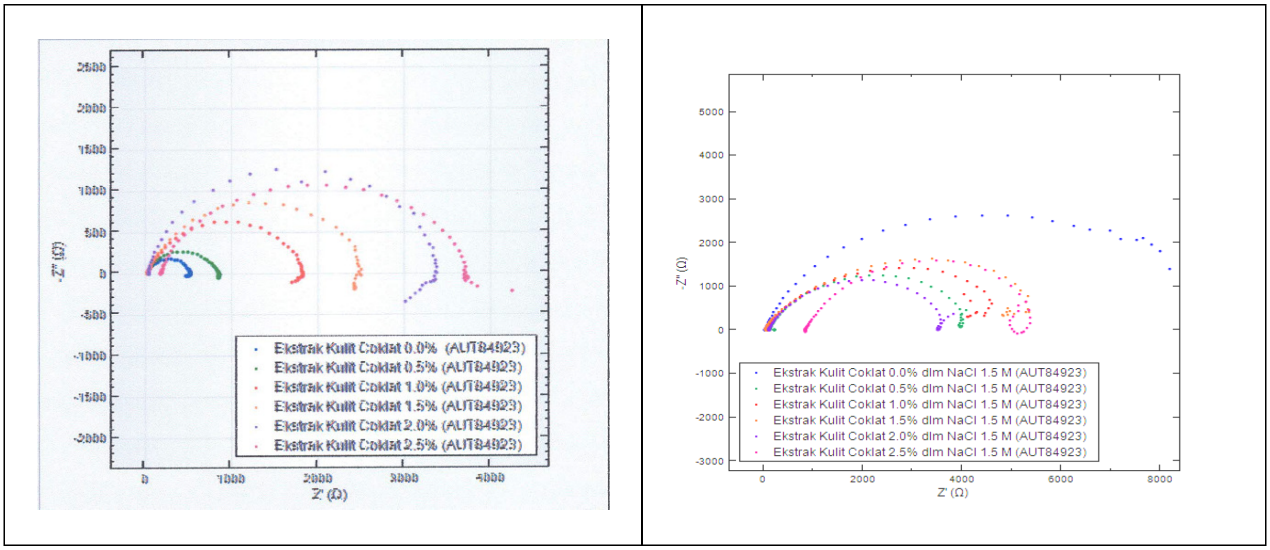


Fig.-5: Nyquist plot of mild steel in presence of *Theobroma cacao* peels extract in (a) HCl 1.5M and (b) NaCl 1.5M

Table-4: Electrochemical and Impedance Parameters of mild steel in the presence of *Theobroma cacao* peels extract in HCl 1.5M

Media corrosive	Inhibitor Conc. (% in v/v)	I_{corr} (mA cm^{-2})	E_{corr} ($Vdec^{-1}$)	Tafel slope ($Vdec^{-1}$)		Rp Ωm^2	IE (%) Icorr	IE (%) Rp
				b_a	bc			
	Blank	0.0631	-0.2800	2.4000	1.7100	6.8707	-	-
	0.5	0.0159	-0.2750	2.8000	2.3000	34.4754	74.8100	80.0700
	1.0	0.0126	-0.2500	3.6700	2.5700	52.0520	80.0300	86.6000
HCl 1.5M	1.5	0.0079	-0.2000	2.0000	1.6000	57.3545	87.4800	88.0200
	2.0	0.0066	-0.2200	5.2500	2.6300	115.2546	89.5400	94.0400
	2.5	0.0050	-0.2800	5.7100	2.6700	157.9865	92.6800	95.6400
	Blank	0.0600	-0.2700	1.8000	1.1400	7.2800	-	-
	0.50	0.0500	-0.2800	3.6000	2.8000	13.3300	18.7000	45.3900
NaCl 1.5M	1.00	0.0500	-0.2200	6.0000	3.7500	21.4600	25.8300	66.0700
	1.50	0.0300	-0.2100	5.0000	2.5000	27.6600	29.1700	73.6900
	2.00	0.0200	-0.2100	5.6000	3.2000	39.6700	68.3000	81.6500
	2.50	0.0100	-0.2200	4.7000	2.2500	74.2400	85.9000	90.1900

Performance evaluations of *Theobroma cacao* peels extract using weight loss and electrochemical measurements

Both techniques are best suited for the corrosion inhibition of *Theobroma cacao* peels extract on mild steel surface. However the value of inhibition efficiency calculated from electrochemical measurement are lower than those obtained from weight loss data (Figure-6). The difference of inhibition efficiency in different techniques can be attributed to the fact that weight loss method gives average corrosion rates which electrochemical gives instantaneous corrosion rate that can be shown in Figure 6. The difference may be expected to arise because of the difference in time required to form an adsorbed layer, which brings down corrosion.

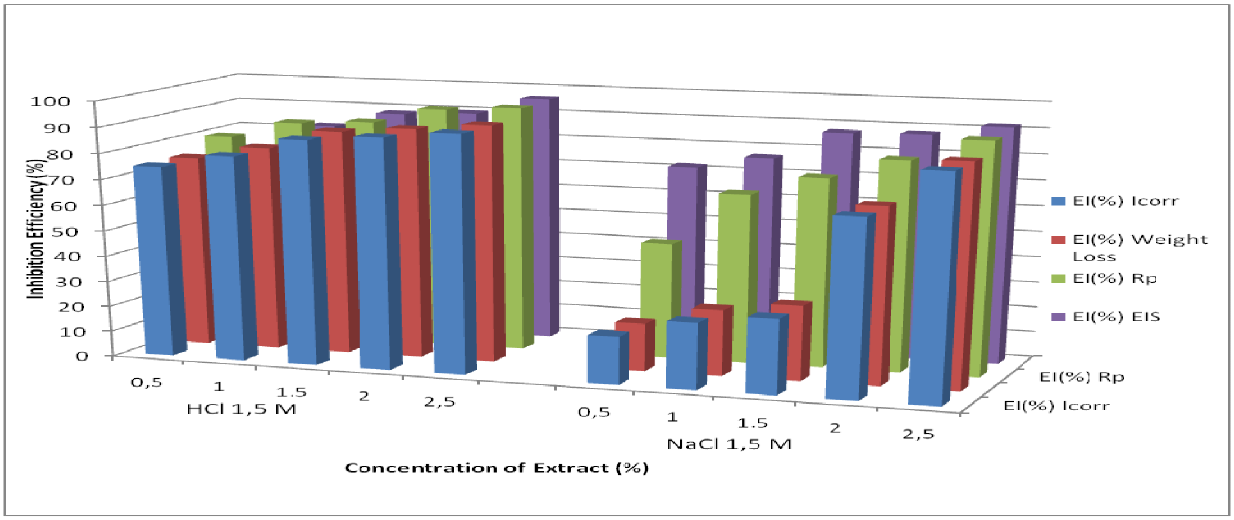


Fig.-6: Comparison between conventional method and electrochemical techniques of *Theobroma cacao* peels extract in HCl and NaCl 1.5M

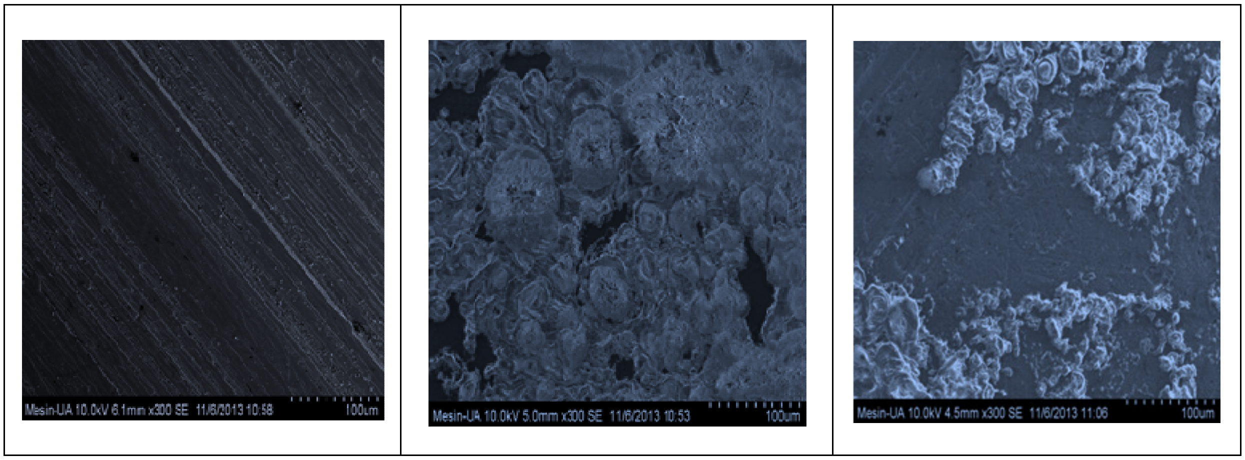
Mechanism of inhibition process

The mechanism of inhibition of corrosion is generally believed to be due to the metal surface. The polar units (*i.e.*) heteroatom like N, O, S *etc*., present in the inhibitor are acting as reaction centre for adsorption process. Referring the chemical compounds identified in *Theobroma cacao* peels extract presented in Table-1, it can be seen that most of the compounds identified are oxygen containing compounds. The hetero oxygen atom in the structure makes its adsorption possible by co-ordinating type linkage through the transfer of lone pairs of electron of oxygen atoms to the vacant *d*-orbitals of metal surface atoms, giving a stable chelate five or six member ring with ferrous ions[30]. The simultaneous adsorption of oxygen atoms forces the *Theobroma cacao* peels extract molecule to be horizontally oriented at the metal surface, which led to increase the surface coverage and consequently protect efficiency even in low inhibitor concentration. The adsorption between the metal and organic constituents of the extract might be through electrostatic interaction.

Analysis of the surface of the mild steel and the formation of a passive layer on its surface in HCl 1.5M and NaCl 1.5M were immersed for 32 days without and with inhibitor cacao peels extract studied using SEM as can be seen in Figure-7 and 8. The image shows a picture of mild steel surface in HCl and NaCl in the absence of a polar extract of cacao peels and pit corrosion products formed hole. But the presence of the cacao peels extract can minimize corrosion products and pits on the surface of the steel by forming a passive layer on the surface. It is functioned as a barrier layer (barrier) against corrosive ions on the surface of mild steel so that electrochemical reactions are slow and eventually corrosion rate will also be reduced[28].

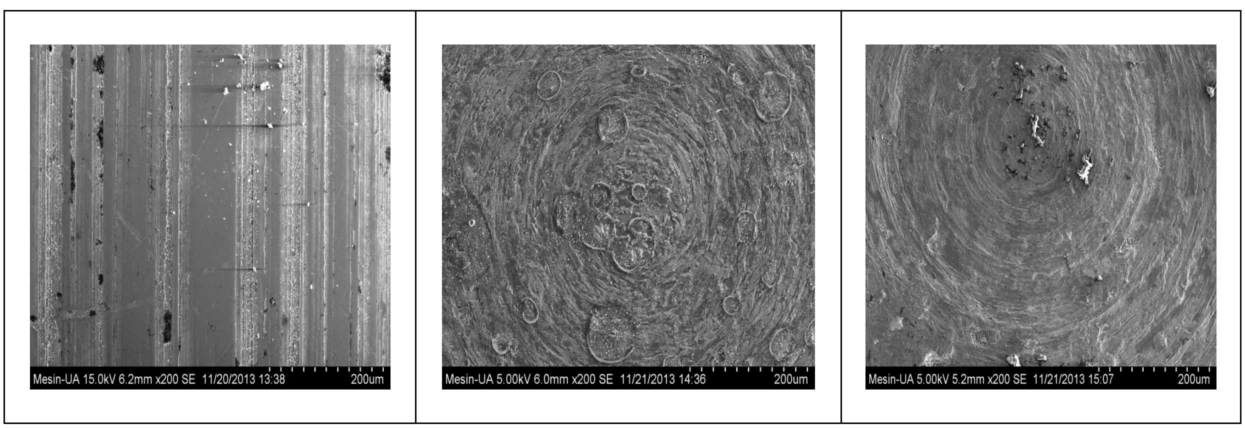
Morphology of Surface Analysis of SEM-EDX

Analysis of elements of C and Fe on the surface of mild steel in HCl 1.5M and NaCl 1.5M was immersed for 32 days with and without extract of cacao peels studied with SEM-EDX. The results of the analysis can be seen in Table-5. It is formed based on the graph obtained atomic percentage of the element C increased in the presence of cacao peels extract. This proves that the C atoms of the molecule cacao peels extracts adsorbed on the steel surface to form a passive layer on the surface of mild steel[29]. While the percentage of atoms of the element Fe decreased in the presence of cacao peels extract. This indicates that the Fe is used to form complex compounds with polar extract of cacao peels so that the percentage of Fe atoms were detected becomes smaller[30]. While the elements which were detected in the initial O in Table 5 does not exist, and extract adding is detected with a low percentage. While in Table 5 an increasing of oxygen percentage and due to the corrosive medium is immersed in HCl 1.5M and NaCl 1.5M without inhibitor, so that the oxide formed quickly by the attack of corrosive ions from HCl and NaCl. But the inhibitors of cacao peels extract which attacks the corrosive ions are capable to prevent corrosion by forming a passive layer in the form of organo-metallic complexes on the surface of mild steel[29, 30.] So that the corrosion rate decreases and fewer oxides formed as evidenced from the percentage becomes decrease to O levels as is shown in Table-5. Recapitulation of elements and oxides were identified in the SEM-EDX testing shown in Figure-5.



(a) (b) (c)

Fig.-7: SEM images of mild steel in HCl 1.5M after 8 days immersion at room temperature (a) before immersion (polished), (b) without extract (blank), and (c) with 2.5 % extract



(a) (b) (c)

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

Table-5: Recapitulation of elements and oxides are identified on SEM-EDX testing

No	Treatment	Content Elements (Wt %)		
1.	Mild steel	0.32	91.43	-
2.	Mild steel + Extract 2.5%	11.50	82.13	5.54
3.	Mild steel + HCl 1.5M	8.57	23.80	66.89
4.	Mild steel + HCl 1.5M + Extract 2.5%	26.40	36.14	34.54
1	Mild steel	0.32	98.79	-

2	Mild steel + Extract 2.5%	6.19	92.66	2,33
3	Mild steel + NaCl 1.5M	2.27	80.61	17.16
4	Mild steel + NaCl 1.5M + extract 2.5%	5.58	80.00	14.54

CONCLUSION

The *Theobroma cacao* peels extract was proved to be a potential inhibitor for mild steel in HCl 1.5M and NaCl 1.5M. The inhibition efficiency increases with inhibitor concentration, time and temperature. Experimental results are well fitted into Langmuir adsorption isotherm. Kinetic and thermodynamic parameters infer the strong adsorption of inhibitor molecule on mild steel surface and also the inhibition is by spontaneous comprehensive adsorption (physical and chemical adsorption) of inhibitor on mild steel surface. Electrochemical measurements confirm the mixed mode of inhibition. Thus *Theobroma cacao* peels extract was proved to be an effective eco friendly and low cost inhibitor.

ACKNOWLEDGMENT

The first author thanks to Ministry of Education, Republic of Indonesia, for BPPS scholarship grant during her doctoral study, and part of this work is supported by former DP2M DIKTI under Hibah Disertasi Doktor Research Grant no. 398/PL9.1.4/LT/2013. Corresponding authors also thank to Andalas University for supporting some experimental works and publications under Hibah Klaster Guru Besar Grant with contract no. 017/UN.16/UPT/2016.

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[RJC-1491/2016]