CORROSION INHIBITION OF MILD STEEL IN 1M HCL BY CATECHIN MONOMERS FROM COMMERCIAL GREEN TEA EXTRACTS

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ABSTRACT

The inhibitory effect of two Indonesian green tea extracts (containing various catechins) were investigated on the corrosion of mild steel (MS) in 1M HCl medium. The anticorrosion effect was evaluated by conventional weight loss method, potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) studies and scanning electron microscopy (SEM) technique. The results evidenced that both the tea extracts act as a good corrosion inhibitor and the inhibition efficiencies (% IE) were in good agreement for all the studies. Adsorption of green tea extract constituent was found to follow Langmuir adsorption isotherm and the calculated Gibb's free energy values indicated the physisorption of inhibitor over the mild steel surface. SEM - EDX studies show the adsorption of catechin monomers which forms a protective layer over the mils steel surface. High performance liquid chromatography (HPLC) analysis was carried out to quantify the catechin fractions in the tea extract and it was found that eight catechin monomers were present in both tea extracts. From all of monomers, it was found that four monomers were identified as components responsible for controlling the dissolution of mild steel in 1 M HCl medium.

Keywords: *mild steel, corrosion inhibition, green tea, HPLC, potentiodynamic, EIS*

I. INTRODUCTION

Tea is one of the most frequently consumed beverages in the world, dating back to more than 5000 years ago. Numerous studies have recorded the beneficial effects of tea, e.g., reducing the risk of cancer, preventing arteriosclerosis (Kakuda, 2002), antiallergic action (Sano *et al.*, 1999), antimicrobial properties (Hamilton-Miller, 1995), lowering the risk of stomach cancer (Setiawan *et al.*, 2001), oesophagus (Hara, 2006), and lung cancer (Zhong *et al.*, 2001). Previous studies have shown that green tea consists predominantly of flavan monomers namely (+)-catechin, (+)-epicatechin and alkaloids (Taniguchi *et al.*, 2007). Interestingly, catechin also exhibits anti-oxidative activity which could reduce oxidation, corrosion, deterioration and discolouration processes (Kyung & Yinzhe, 2006).

Corrosion is a common phenomenon in industries and it attracts considerable amount of interest because of its hazardous nature on metals (Bothi *et al.*, 2010). In many industries, acid solutions are frequently used for acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes (Fan *et al.*, 2002; Hosseini *et al.*, 2007; Shahrabi *et al.*, 2007) which leads to corrosive attack of metals. Generally, the inhibitors are used in these processes to control the metal dissolution as well as the acid consumption. Most of the inhibitors are organic molecules (Nmai, 2004) however inorganic molecules (Kiehl & Brendel, 2002) and polymeric materials (Kalendová *et al.*, 2008) are also used. Although high anticorrosion potential was exhibited by many organic molecules, they pollute the environment during their synthesis and applications (Raja & Sethuraman, 2008).

Natural products are being studied for their corrosion inhibition potential as they are more environmentally friendly, showing good inhibition

efficiency with low risk of environmental pollution (Duke *et al.*, 2000; Rahim & Kassim, 2008). The use of natural compounds from plant extracts rich in tannins (Rahim *et al.*, 2008), *Rauvolfia serpentine (Bothi Raja & Sethuraman, 2009b)*, black pepper extract (Bothi Raja & Sethuraman, 2008), *Lawsonia* (El-Etre *et al.*, 2005), *Opuntia* extract (El-Etre, 2003) have been widely reported by several authors.

Anticorrosion potential of tea wastes (Sethuraman *et al.*, 2001), as well as its constituent caffeine (Anthony *et al.*, 2004; Fallavena *et al.*, 2006) had been successfully reported earlier. These studies concluded that the heterocyclic atoms of the caffeine molecule are responsible for its anticorrosion potential. The present study was inspired by the reports that green teas are characterised by the presence of catechin monomers that have been studied individually, which coincidentally are effective corrosion inhibitors (Hosseini *et al.*, 2003; Ashassi-Sorkhabi *et al.*, 2005). Thus this work aims at investigating the anticorrosion potential of a natural product viz., catechin monomers derived from green tea extracts on MS in 1 M HCl medium. The assessment of the corrosion behaviour has been studied using weight loss, EIS, potentiodynamic polarisation measurements, IR spectroscopy and the morphology of inhibited mild steel surface analysed by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX). High performance liquid chromatography (HPLC) has been utilised identify and quantify the active components of the green tea extracts simultaneously that are consumed during the corrosion inhibition process.

II. EXPERIMENTAL

A. Inhibitor preparation

Two Indonesian green tea samples (*Camellia sinensis*) were purchased from a local supermarket. The green tea samples (10 g) were extracted in 100 mL acetone 70% for 24 h at 80°C by using hot plate method (Row & Jin, 2006). The extract was cooled and centrifuged at 4000 rpm for 5 min. The sample was evaporated and the resulting gummy material obtained was dried and grinded. Various concentrations of the tea extracts were prepared by dissolving known quantities of the resultant powder in 1 M HCl.

B. Specimen preparation

The MS specimens of composition (Fe: 97.57, C: 1.54, O: 0.88% weight) were taken and were polished using different grades of abrasive paper from 400 up to 1200 before the analysis. MS specimens of size (2.7 x 2.7 x 0.1 cm) were used for the weight loss method and SEM analysis while specimens with an exposed area of 3.142 cm² were used for the electrochemical studies.

C. Weight loss method

The experiment was carried out in a beaker containing 100 mL test solution. A clean pre-weighed MS specimen was completely immersed in 100 ml of electrolyte with and without the addition of different concentrations of GT extract at room temperature (30° C ± 2). After 24 h of immersion in 1 M HCl solution, the specimen was withdrawn, rinsed with distilled water, washed with acetone, dried and weighed. Triplicate measurements were performed. The inhibition efficiency (% IE) was calculated as follows:

$$\% \ IE = \left(1 - \frac{W_i}{W_0}\right) \times 100 \qquad \text{............................... (1)}$$

Where,

W_0 and W_i are the weight loss of mild steel without and with inhibitor, respectively.

D. Electrochemical method

Electrochemical studies were carried out using Gamry Instrument reference 600 (potentiostat/galvanostat/ZRA). A three-electrode cell system were employed for the measurement wherein mild steel with an exposed area of 3.142 cm² acts as a working electrode (WE) while platinum wire and saturated calomel electrode acts as counter electrode and reference electrode (SCE), respectively. The measurements were performed in 1.0 M HCl solution with and without the addition of different inhibitor concentrations in an aerated environment. All polarisation and impedance curves were recorded at room temperature (30±2)°C and the electrodes were immersed in the test solution for 30 min at natural potential to attain steady state before measurement. AC impedance measurements were carried out at the corrosion potential (E_{corr}) with frequency

ranging from 0.1 to 10000 Hz at an amplitude of 10 mV. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (% IE) is calculated from the charge transfer resistance (R_{ct}) values by using equation (2):

$$\% \ IE = \left(1 - \frac{R_{ct(o)}}{R_{ct(i)}} \right) \times 100 \quad .... (2)$$

Where, $R_{ct(o)}$ and $R_{ct(i)}$ is the charge transfer resistance of mild steel without and with inhibitor, respectively.

The potentiodynamic current density - potential curves were recorded by scanning the electrode potential from -800 to -200 mV (vs SCE) with a scanning rate of 1 mV s^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). Equation (3) shows the calculation of % IE from the I_{corr} values.

$$\% \ IE = \left(1 - \frac{I_{corr(i)}}{I_{corr(o)}} \right) \times 100 \quad .... (3)$$

Where, $I_{corr(i)}$ and $I_{corr(o)}$ is the corrosion current density of mild steel with and without inhibitor, respectively.

E. FTIR spectroscopic analysis

The green tea extracts were analysed by Fourier transformed infrared (FTIR) spectroscopy for the identification of the functional groups. The FT IR study was carried out by using the Perkin Elmer System 2000 FT IR instrument in the IR range 400-4000 cm^{-1}. The pellet for the solid sample was prepared by using KBr pellet method with the ratio of the sample to KBr was 1:10. The mixture was then pressed with 8-ton pressure to obtain a palette. The acquiring of the spectra and peaks assignment was performed using FTIR software Spectrum Version 3.02.01.

F. Scanning electron microscopy (SEM)

Surface analysis was conducted on the MS surface before and after the electrochemical measurements. After the electrochemical measurements, the MS specimens were removed, slowly rinsed with distilled water and dried. The analysis was performed using SEM LEO SUPRA 50VP instrument.

Table 1
Effect of green tea extracts for the corrosion of mild steel in 1.0 M HCl (Weight loss studies)

Inhibitor	Concentration (ppm)	Weight loss (g)	% IE (wt%)
-	0	0.0448	-
GT 1	50	0.0231	48.44
	100	0.0184	58.93
	150	0.0144	67.85
	200	0.0121	75.22
GT 2	50	0.0220	50.89
	100	0.0171	61.83
	150	0.0133	70.31
	200	0.0893	79.24

IE, inhibition efficiency; GT, green tea

G. High Performance Liquid Chromatography (HPLC) analysis

The HPLC system used consisted of two LC-10 AD VP pumps for high-pressure gradient elution attached with a SPD-10Avp UV detector (Shimadzu, Japan). The mobile phase composition comprises of water: acetonitrile: methanol (83:6:11). The column used was a monolithic Rp–18 e 100–4.6 mm (Merck KGaA, Germany). Signals were monitored at 280 nm. Standard solutions and tea samples were filtered through a 0.45 μm acrylic polymer filter before being injected into the HPLC unit. Quantification was done using the external calibration method where peak areas versus concentrations were plotted. Linear least-square analysis on the straight line was used for the quantification, while qualitative analysis was based on comparison of the retention times of standards. 20 μL of the analytical samples were injected.

III. RESULTS AND DISCUSSION

A. Weight loss measurement

The % IE obtained for different concentrations of green tea extract is depicted in Table 1.

The results show a positive correlation between the concentration of green tea extract and the inhibition efficiency for mild steel in 1 M HCl solution. This trend may result from the fact that

the amount adsorbed and the coverage of inhibitor molecules on the mild steel surface increased with the increase of the green tea extract concentration, thus the mild steel surface is efficiently blocked from the hydrochloric acid. The maximum % IE was obtained at maximum concentration of 200 mg L^{-1} for both green tea extracts and was found to be 75.22 and 79.24 % for GT 1 and GT 2, respectively.

B. Potentiodynamic polarisation measurements

The various corrosion parameters viz., corrosion potential E_{corr}, corrosion current density I_{corr}, cathodic (β_c), anodic (β_a) Tafel slopes and (IE) were calculated using the intersection of the anodic and cathodic Tafel lines and are given in Table 2.

It is clear from the potentiodynamic experimental results that the presence of tea extracts reduces the corrosion current density, I_{corr}, which is an indication of the decrease in the corrosion rate. The decrease in I_{corr} values is due to the decrease of the aggressive acid attack on the mild steel surface, attributed to the adsorption of inhibitor molecule. Furthermore, the additions of tea extract shift the corrosion potential to the positive side, due to the decrease in the anodic reaction. This indicated that the inhibitors were adsorbed on the anodic sites of the mild steel surface, which prevented the metal dissolution reaction and thus controlling the corrosion process. However, the Tafel constants β_c and β_a did not change significantly with inhibitor concentrations, indicating that
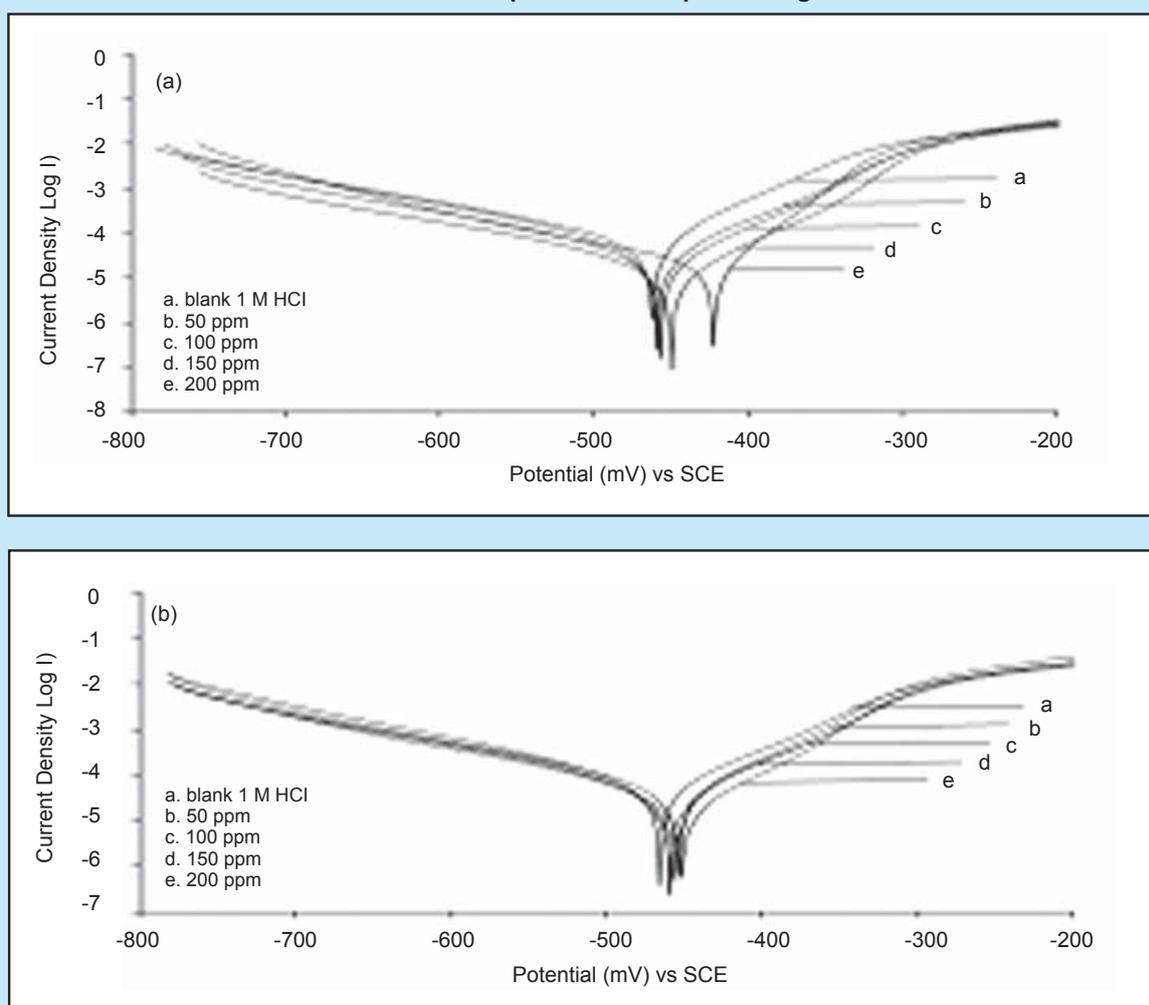

Figure 1
Tafel plots of (a) GT 1, and (b) GT 2 extracts on mild steel in 1 M HCl

Table 2
Effect of green tea extracts for the corrosion of mild steel in 1.0 M HCl
(Polarization studies)

Inhibitor	Concentration (ppm)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	% IE
-	0	-484	386	88.7	147.9	-
GT 1	50	-477	158	87.3	152.5	59.07
	100	-468	136	40.4	54.1	64.77
	150	-461	94	32.5	34.8	75.65
	200	-452	78	30.1	32.1	79.79
GT 2	50	-482	132	86.8	155.9	65.80
	100	-468	111	85.7	143.6	71.24
	150	-455	77	78.3	132.1	80.05
	200	-442	62	42.2	114.3	83.94

GT, green tea; IE, inhibition efficiency

the retardation of the reactions (hydrogen evolution and metal dissolution) was affected without changing the mechanism. The % IE was found to enhance when the concentration of the green tea extract was increased, resulting in maximum of 79.79% for GT 1 and 83.94% for GT 2 extracts, respectively. The results obtained are in good agreement with those obtained from the weight loss measurements.

C. Electrochemical impedance studies (EIS)

EIS analysis shows typical Nyquist plots for GT 1 and GT 2 extracts which are given in Figures 2a and b, respectively.

The impedance parameters, viz., charge transfer resistance (R_{ct}), and constant phase element (CPE) were calculated by analysing the impedance plots using the equivalent circuit (Figure 3) and the values are listed in Table 3.
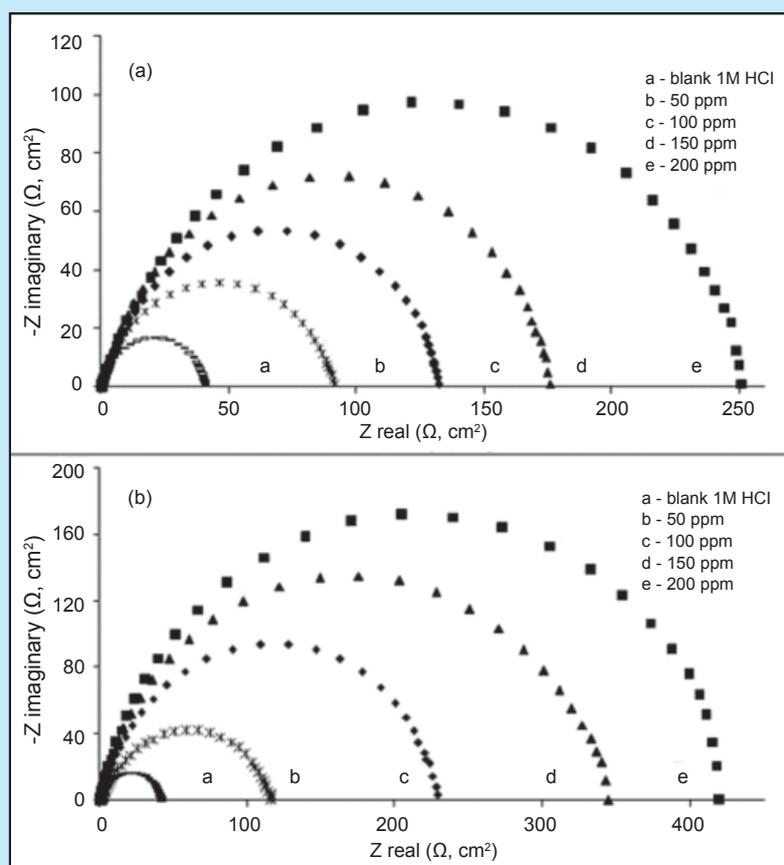

Figure 2
Nyquist plots of (a) GT 1, and
(b) GT 2 extracts on mild steel in 1 M HCl

The usefulness of these data permits the analysis of the alternating current (AC) impedance data, which are based on the modelling a corrosion process by an electrical circuit (Hussin & Kassim, 2010).

From Figures 2a and b, it was observed that the Nyquist plots showed slightly depressed semi-circular shapes with only one time constant and the diameters of the capacitive loop increased with increasing inhibitor concentration. This indicates the increasing coverage of the metal surface and also signifies a charge transfer process as the main controlling factor in the corrosion process (Benabdellah *et al.*, 2007).

Further, it is also observed from Table 3 that the R_{ct} values increased with increasing concentrations of inhibitors. This is because, the addition of inhibitor increases the adsorption of phyto-constituents over the MS surface and results in the formation of a protective layer which may decrease the electron transfer between the metal surface and the corrosive medium. The values of CPE decrease with the increase in inhibitor concentrations due to the addition of inhibitor that increases the adsorption phenomena, which consequently may decrease the electrical capacity and/or increase in the thickness of the electrical double layer (Bentiss *et al.*, 2007). The % IE of impedance results, are in good agreement with the polarisation and weight loss studies that shows maximum of 83.47 and 89.96% for GT 1 and GT 2 extracts, respectively for the maximum concentration of 200 g mL⁻¹.

D. Adsorption isotherm

To examine the adsorption behaviour of the green tea extracts on the MS surface in 1 M HCl medium, the adsorption isotherm was plotted. The dependence of the fraction of the surface covered (θ) obtained by the ratio of E/100 as a function of the logarithm of the concentration (log C) of tea extracts was tested graphically by fitting it to several adsorption isotherms. The experimental data from all measurements was found to fit well with the Langmuir adsorption isotherm and are depicted in Figures 4a, b and c for weight loss study, polarization

Table 3
Effect of green tea extracts for the corrosion of mild steel in 1.0 M HCl (Impedance studies)

Inhibitor	Concentration (ppm)	R_{ct} ($\Omega.cm^2$)	CPE (μFcm^{-2})	% IE
-	0	41.4	48.7	-
GT 1	50	87.6	28.7	52.74
	100	127.8	25.3	67.60
	150	177.1	22.1	76.79
	200	250.6	18.1	83.47
GT 2	50	110.2	33.4	62.70
	100	291.1	28.7	85.88
	150	351.1	21.1	88.21
	200	409.4	18.1	89.96

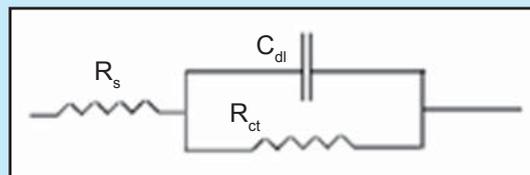*GT, green tea; IE, inhibition efficiency; CPE, constant phase element*

Figure 3
Electrical equivalent circuit for AC impedance measurement

and impedance studies respectively, which obeys (Morad & El-Dean, 2006):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{and} \quad \Delta G^o_{ads} = - RT \ln C_{water} K_{ads} \quad ... (4)$$

Where, C is the concentration of inhibitor, θ is the surface coverage determined by E/100, K_{ads} is the adsorption equilibrium constant and ΔG^o_{ads} is the standard Gibbs free energy, R is molar gas contant, T is the temperature and C_{water} is the concentration of water in 1000 g L⁻¹. The Gibbs free energy values (ΔG^o_{ads}), linear regression coefficient and adsorption – desorption equilibrium constant (K_{ads}) derived from the Langmuir plot are depicted in Table 4.

The negative values of ΔG^o_{ads} revealed the spontaneity of the adsorption process (Hosseini *et al.*,

Table 4
Adsorption isotherm parameters

Inhibitor	Methods	R^2	K_{ads} (L g^{-1})	ΔG^o_{ads} (kJ/mol)
GT 1	Weight Loss	0.9994	13.47	-23.61
	Potentiodynamic	0.9992	23.79	-25.18
	EIS	0.9996	25.41	-25.44
GT 2	Weight Loss	0.9994	18.01	-24.51
	Potentiodynamic	0.9998	26.61	-25.49
	EIS	0.9998	35.79	-26.31

2003). Generally, ΔG^o_{ads} values around −20 kJ mol^{-1} or lower are associated with electrostatic interactions between the charged centers of inhibitors and charged metal surface (physisorption) (Ashassi-Sorkhabi *et al.*, 2005). Values more negative than −40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (Bentiss *et al.*, 2002). The calculated -ΔG^o_{ads} values for all the studies were depicted in Table 4. The -ΔG^o_{ads} values were found to be in the range between -23 to -27 kJ mol^{-1} for both the green tea extracts, which evidenced the typical physisorption of inhibitors on mild steel surface. The higher K_{ads} values obtained for GT 2, suggesting that this inhibitor was more strongly adsorbed onto the MS surface compared to GT 1 (Kardas & Solmaz, 2006).

E. High Performance Liquid Chromatography (HPLC) analysis

The concentrations of the catechin monomers and caffeine in the green tea extracts were determined by using the HPLC technique. This method is by
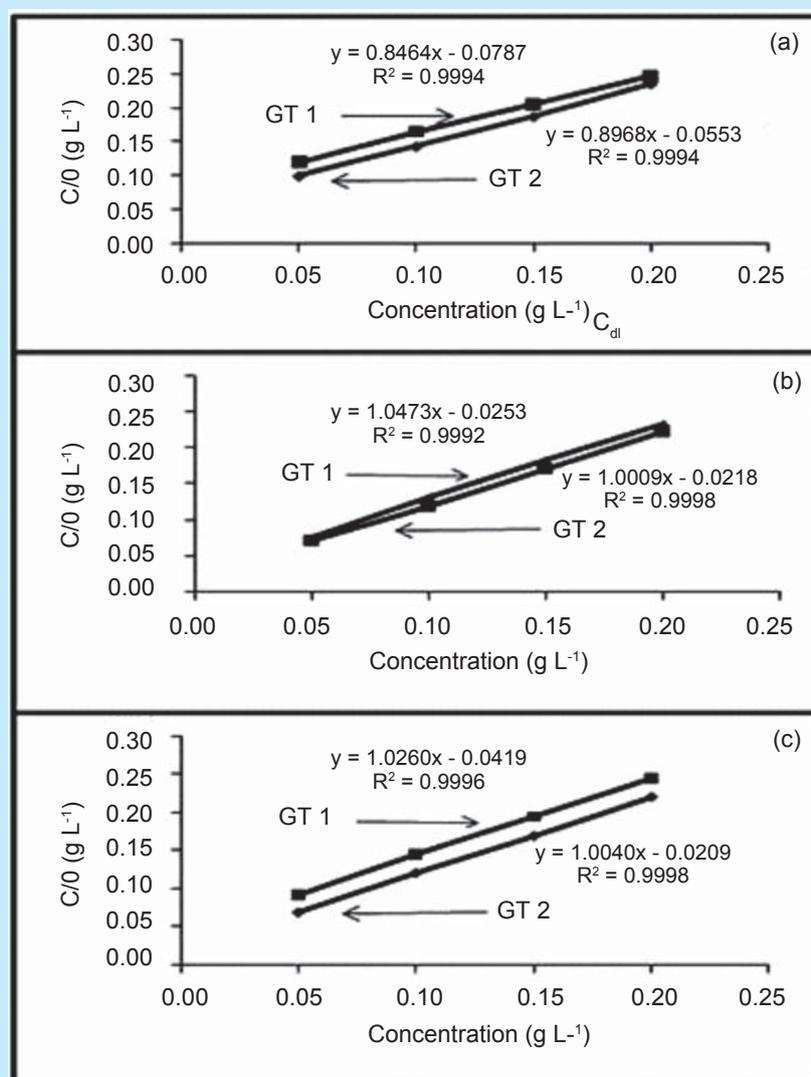

Figure 4
Langmuir adsorption isotherm plots for GT 1 and GT 2 extracts on the mild steel surface from (a) weight loss, (b) potentiodynamic and (C) EIS measurement

far the most popular technique for analysing tea catechins. Wang et al. (2000) reported on the use of methanol/ water and acetonitrile/water as mobile phase for the catechin analysis. The catechin monomers and caffeine were separated in about 40

minutes. In contrast to all previous HPLC analysis that uses particle-type stationary phase, the present study uses a monolithic column. The use of highly porous monolithic columns has resulted in many advantages to the user (e.g., minimum back pressures, faster

Table 5
Determination of catechins and caffeine in green tea samples by HPLC analysis

Analytes	Concentration (mg g^{-1})	
	GT 1	GT 2
GC	3.29 ± 0.43	4.89 ± 0.78
EGC	12.07 ± 0.55	16.22 ± 0.19
C	2.21 ± 0.24	2.47 ± 0.52
Caffeine	33.24 ± 0.38	36.51 ± 0.72
EGCG	30.72 ± 0.45	33.01 ± 0.59
EC	6.12 ± 0.27	7.08 ± 0.29
GCG	2.82 ± 0.13	2.99 ± 0.16
ECG	7.23 ± 0.17	9.21 ± 0.16
CG	0.53 ± 0.07	0.58± 0.08

n = 3, GT, green tea; GC, gallo catechin; EGC,
epigallo catechin; C, catechin; EGCG,
epigallo catechin gallate; EC, epicatechin;
GCG, gallocatechin gallate; ECG,
epicatechin gallate and CG, catechin gallate

Table 6
Consumption of catechin monomers after the corrosion process determined by HPLC analysis

Inhibitor	Catechin monomers	Inhibition consumed (%)
GT 1	EC	3.25±0.11
	EGC	8.83±0.24
	ECG	11.59±0.32
	EGCG	13.26±0.29
GT 2	EC	4.25±0.21
	EGC	10.31±0.19
	ECG	13.66±0.38
	ECGC	16.15±0.27

n = 3, GT, green tea; EGC, epigallo catechin;
EGCG, epigallo catechin gallate; EC,
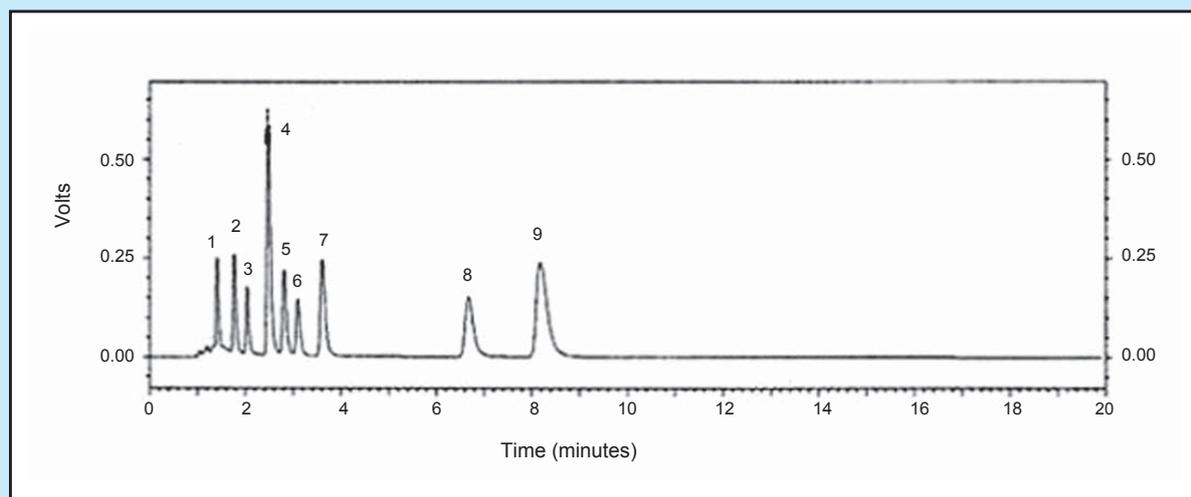epicatechin; ECG, epicatechin gallate

Figure 5
The separation of catechin and caffeine standards mixture (40 ppm) using of water: acetonitrile: methanol (83: 6: 11) as mobile phase. Peak assignment :
(1) (-)-gallocatechin, (2) (-)-epigallo catechin (EGC), (3) (-)-Catechin (C), (4) (-)-caffeine, (5) (-)-Epigallocatechin gallate (EGCG), (6) (-)-Epicatechin (EC), (7) (-)- gallocatechin gallate (GCG), (8) (-)-Epicatechin gallate (ECG), and (9) (-)- catechin gallate (CG)

Figure 6
Structures of catechin monomers and caffeine
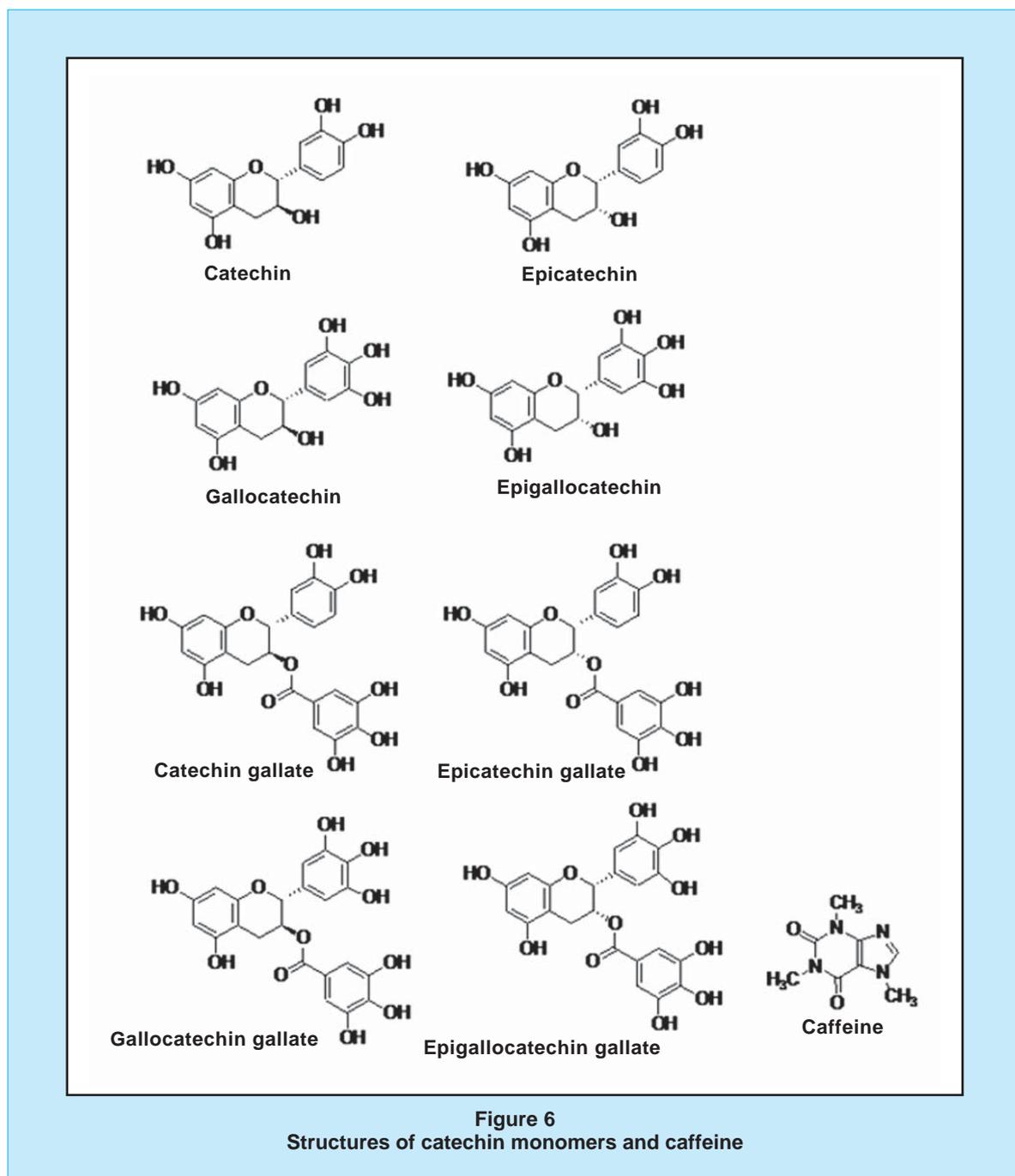
separations, consumption of less mobile phases). In the present study, the optimised isocratic system comprising water: acetonitrile: methanol (83:6:11) as mobile phase was used and satisfactory separation of the catechins and caffeine was obtained using a flow rate of 1.4 mL min^{-1} (Figure 5). All components were separated in about 8 min. The separation was comparatively faster than the previous reports (Fernandez *et al.*, 2000; Wang *et al.*, 2000; Nishitani

& Sagesaka, 2004) that are based on conventional particle-type stationary phase. Nine peaks were observed for the tea extracts and their concentrations are given in Table 5. Based on the retention times, the peaks were identified as gallocatechin (GC), epigallocatechin (EGC), catechin (C), caffeine, epigallocatechin gallate (EGCG), epicatechin (EC), gallocatechin gallate (GCG), epicatechin gallate (ECG), catechin gallate (CG). The order of elution

was: GC > EGC > C > caffeine > EGCG > EC > GCG> ECG > and > CG (Figure 5).

In order to determine the anticorrosion ingredients of tea extracts quantitatively, HPLC analysis of test solutions was carried out before and after the corrosion processes. The concentrations of catechin consumed after the inhibition process from the weight loss measurements are given in Table 6. In all previous reports (Rahim *et al.,* 2007), it was assumed that all monomers would act as inhibitors for steel corrosion and their inhibitive performance depended on their concentrations. However, a key findings of this study was that only certain catechin monomers gave significant contributions to the corrosion inhibition.

Among the eight catechin monomers present in the tea extract, only epicatechin (EC), epigallocatechin (EGC), epicatechin gallate (ECG) dan epigallocatechin gallate (EGCG) were found to be consumed in the inhibition process as witnessed from the reduction of peak areas in the HPLC chromatogram. The order of increasing consumption and thus adsorption is as follows EC < EGC < ECG < EGCG. The peak areas for the other components were virtually unchanged. Interestingly, none of the chiral counterparts [(C), (GC), (GCG) and (CG)] were found to participate in the inhibition process although some of these monomers have shown inhibitive effect when used individually (Rahim *et al.,* 2007). This suggests that the inhibition is stereospesific and the (R, R) conformation. (Figure 6) may have facilitated the absorption of these molecules. The higher catechin content of the GT 2 extract showed higher consumption of the monomers, which is consistent with the higher inhibition efficiency of the GT 2 extract as compared to the GT 1 extract. The amount of monomers consumed also showed a positive correlation with the time of immersion when higher consumption of monomers was recorded for the weight loss method. Surprisingly, although both green tea extracts had the highest caffeine content, the HPLC results did not show the consumption of caffeine alkaloid. This contradicts to the earlier studies that reported caffeine as an effective metal corrosion inhibitor (Anthony *et al.,* 2004). This disparity could be due to the fact that the presence of the catechin monomers (EC, EGC, ECG and EGCG) may have blocked the adsorption of caffeine molecule over the MS surface or due to the different electrolyte used. The structures of the various catechins and caffeine are shown in Figure 6.

F. FT IR studies

The green tea extracts were studied by FTIR spectroscopy in order to identify the functional groups. Figure 7 shows the IR absorption spectrum of the green tea extracts and the typical functional groups of catechin namely O-H, C=C (for aromatic rings) and C-O that were evidenced at 3400-3100, 1600 and 1150 – 1010 cm^{-1}, respectively (Maoela *et al.,* 2009). These are the functional groups that were already identified as potent anticorrosion groups in organic corrosion inhibitors as reported by many researchers (Blustein *et al.*, 2006).

It was assumed that a catechin monomer which has more numbers of hetero functionality and π − electronic clouds could serve as a better corrosion inhibitor. According to this consideration, Epigallocathecin gallate (EGCG) monomer was assumed to contribute more during the corrosion
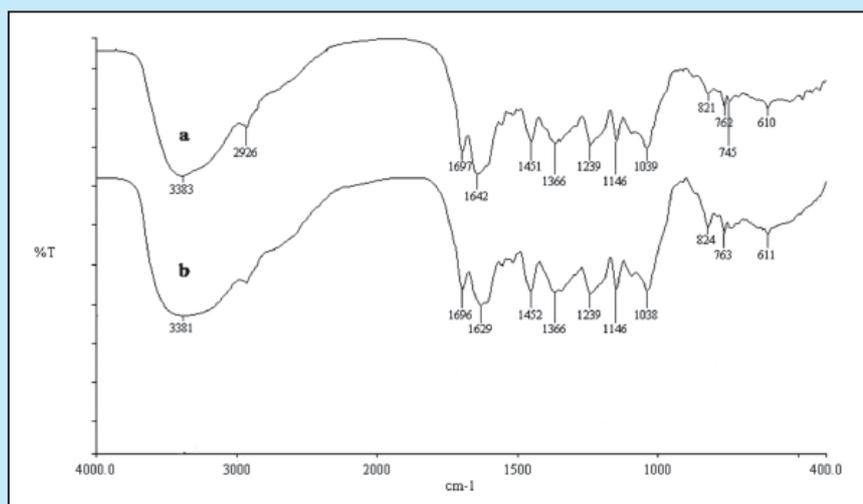

Figure 7
IR spectra of (a) GT 1, and (b) GT 2 extracts.

inhibition process since it has three aromatic rings along with eight OH groups while ECG contains seven OH groups and EC, EGC having less numbers of aromatic rings and OH groups. Indeed, as mentioned earlier, HPLC results showed that EGCG monomer was consumed the most during the inhibition process, suggesting that the presence of hetero functional groups (OH) and π - electrons on the benzene ring contributed to the corrosion inhibition by EGCG.

G. Scanning Electron Microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDX) studies

To monitor the morphological changes on the MS surface during the corrosion process, SEM – EDX studies were carried out. MS specimens were screened after the potentiodynamic polarisation studies and the micrographs are given in Figures 8a, b and c. From Figure 8a.

It is clearly seen that the surface is very rough and severely damaged in the absence of inhibitors while in Figures 8b and 8c the surfaces are transformed into smoother, more uniform deposits upon addition of the green tea extract. The distribution of rough surfaces were significantly reduced. The composition of the sample from the EDX analysis showed the increase of carbon and reduction of oxygen atoms due to the reduction of corrosion products (Table 7), probably due to the adsorption of the monomers of the green tea extract.

IV. CONCLUSIONS

The two commercial Indonesian green tea extracts showed comparable inhibition properties for the corrosion of mild steel in 1 M HCl medium. The % IE obtained via polarisation measurement is in good agreement with

Table 7
The composition of samples from the EDX analysis

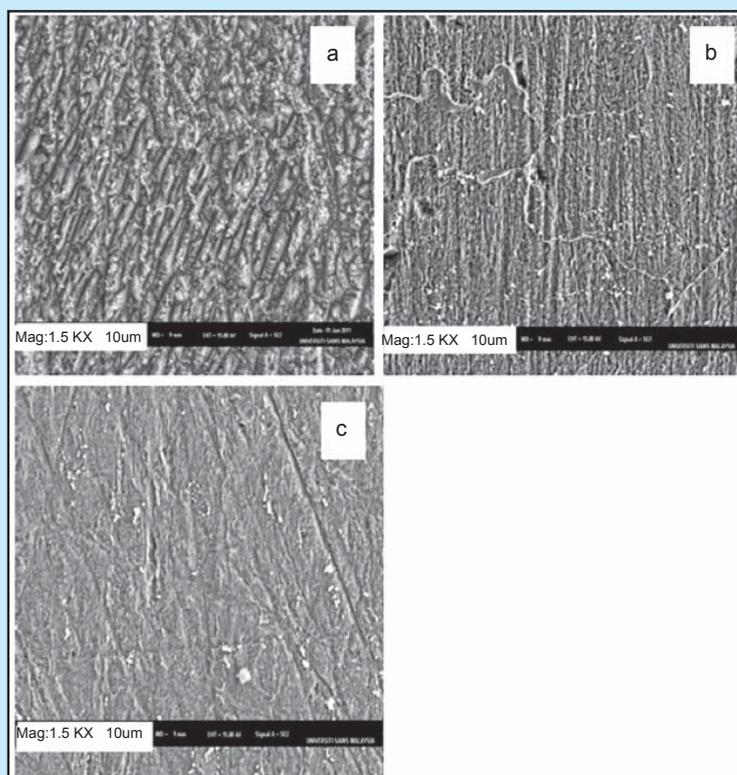| Sample	Element (%)		
	Fe	O	C
Fresh mild steel	97.57	0.88	1.54
Mild steel without inhibitor	74.23	23.54	1.41
Mild steel with GT 1 extract	89.21	7.45	4.81
Mild steel with GT 2 extract	90.68	5.79	4.07

GT – green tea

Figure 8
SEM images of mild steel in 1M HCl medium
(a) absence of inhibitor (b) GT 1, and (c) GT 2 extracts

that obtained by using the weight loss and impedance methods. The polarisation results also revealed that both inhibitors control the corrosion through mixed mode of inhibition. SEM - EDX studies show the adsorption of catechin monomers which forms a protective layer over the MS surface. Both the tea extracts were found to obey the Langmuir adsorption isotherm and the thermodynamic parameters prove the physical adsorption of the phytoconstituents. The HPLC

technique proved to be an indispensable tool for the simultaneous determination of the active components of the green tea extracts that are responsible for the inhibition of MS corrosion.

V. RECOMMENDATION

The HPLC technique has proven to be an essential tool for simultaneous determination of catechin monomers that are responsible for the corrosioninhibition of mild steel. This technique can be used to explore different corrosion inhibition mechanism for various corrosive media viz., H_2SO_4, basic electrolytes (e.g, NaOH) and neutral electrolytes (e.g, NaCl) as well as for various metals viz., Zn, Cu dan Al. The active constituents from other natural products containing alkaloids, flavonoids and polyphenols for corrosion inhibition of metals can be similarly determined. In addition, through the same technique, the antioxidant studies of these plant extracts can be correlated to the corrosion inhibition properties.

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