

GAMBIR EXTRACT AS A CORROSION INHIBITOR FOR MILD STEEL IN ACIDIC SOLUTION

Nofrizal

“LEMIGAS” R & D Centre for Oil and Gas Technology

Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA

Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Faxsimile: 62-21-7246150

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ABSTRAK

Pengaruh penghambatan korosi baja lunak menggunakan ekstrak Gambir pada medium asam klorida 1M dipelajari menggunakan metode pengukuran kehilangan berat, polarisasi potensiodinamik, spektroskopi impedansi elektrokimia (EIS) dan mikroskop elektron (SEM). Hal ini diyakini bahwa senyawa fenolik yang terkandung pada ekstrak Gambir dalam media asam klorida encer dapat bertindak sebagai penghambat proses korosi. Penelitian laju korosi ini menunjukkan bahwa ekstrak Gambir memberikan jenis penghambatan korosi melalui anodik proses, dimana konsentrasi optimum ekstrak gambir dalam menahan laju korosi adalah 150 ppm. Effisiensi penghambatan laju korosi untuk metode pengukuran berat badan, pengukuran polarisasi potensiodinamik dan spektroskopi impedansi elektrokimia berturut-turut adalah 76,52; 88,28 dan 66,27 %. Analisis SEM menunjukkan bahwa terdapat perbaikan bentuk morfologi baja ringan yang telah direndam dengan ekstrak gambir.

Kata kunci: Korosi, Gambir, polarisasi potensiodinamik

ABSTRACT

The inhibition influence of Gambir extract in 1M Hydrochloric Medium on corrosion of mild steel in acidic solution was studied by weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM) method. It is believed that the phenolic compounds that contained in the Gambir extract in 1 M Hydrochloric medium to be responsible for the inhibition. The corrosion studies shows that Gambir extract gives an anodic type of inhibition and best at the concentration of 150 ppm. The inhibition efficiency for weight loss measurement, potentiodynamic polarization measurement, and electrochemical impedance spectroscopy were 76.52, 88.28 and 66.27% respectively. SEM analysis shows that the morphology of inhibited mild steel was improved compared with uninhibited mild steel.

Keywords: Corrosion, Gambir, Potentiondynamic Polarisation

I. INTRODUCTION

Gambir is an aqueous extract prepared from the leaves and young twigs of *Uncaria Gambir* Roxb, a member of the Rubiaceae family^[1]. Gambir can be found in irregular masses or cubes, reddish-brown, pale brownish-gray, gray or light brown. It can be easily broken into small fragments or reduced to powder, bitterish with sweetish after-taste, inodorous and great astringency^[2].

In the present day, the usage of gambir has been diversified due to its local anesthetic property. Gambir

has been employed as an astringent medicine in Southeast Asia for the treatment of diarrheas and sore throat^[3]. Previously, gambir was used to cure spongy gums and tooth acne by placing it in the affected area instead of chewing it with a betel nut^[2].

Taniguchi *et al.*^[3] showed that gambir consists of flavan monomers, (+)-catechin and (+)-epicatechin, several other dimeric compounds related to (+)-catechin, as well as alkaloids. Recently, plant extracts have become important as an environmentally acceptable, readily available and renewable source

for a wide range of corrosion inhibitor. Several investigations have been reported using plants extract and showed that the actual inhibitors in the plants extract are usually alkaloids, polyphenolic compounds as well as carbohydrates^[5, 6].

Corrosion is known as physicochemical interaction between a metal and its environment that results in metal deterioration or surface damage. It is often called rust^[7, 8]. Temporary existence in metallic form causes metal to corrode with the presence of driving force^[9]. In general, corrosion can be chemical or electrochemical. Chemical corrosion is direct oxidation of the metal. The reactions involve at least one anodic and one cathodic reaction. Anodic reactions are oxidation or dissolution reactions in which electrons are released. This reaction occurs on the surface of anode. Whereas cathodic reactions are reduction or deposition reactions in which electrons are consumed, and it is occurred on a cathode.

Corrosion affects every sector of industry as well as the infrastructure and the general population. It can be extremely harmful, bringing physical effect and financial ruin. Corrosion may cost a country billion of dollars each year for replacement and maintenance costs. Due to the increased demand for sustainability and life extension, a great number of scientific studies have been made to investigate corrosion inhibition potential of natural products since these organic compounds with N, S and O showed significant inhibition efficiency^[10].

Corrosion inhibitors are substances that reduce the rate of either anodic oxidation or cathodic reduction or both. It can be anodic, cathodic, or mixed inhibitor. The aim of the present work is to evaluate the inhibitive effect of Acetone extract of Uncaria Gambir as a natural corrosion inhibitor on the corrosion of mild steel in acidic solution. The behavior of the extract was studied using weight loss, potentiodynamic polarization methods, electrochemical impedance spectroscopy and the inhibited mild steel surface was examined using SEM.

II. MATERIALS AND METHODS

A. Sample Preparation

Raw materials of gambir purchased from Payakumbuh West Sumatera, Indonesia were ground into fine powder and sieved through a 50 μm filter.

Parts from this gambir (5.0 g) were dissolved in $\sim 80^\circ\text{C}$ acetone 40% (100 ml). The aqueous extract of gambir was shaken at 200 rpm (IKA® KS 260) for 1 hour. Then it was transferred to a centrifuge tube and centrifuged for 5 minutes to obtain a clear solution. The undissolved gambir was removed by filtering them through vacuum filter and the mother liquors were treated with n-Hexane (50 ml, QR&C) three times for separation and purification of the extracts. The purified extracts of gambir in water were freeze-dried (Labconco) for 2 days. Finally, the dried extracts were ground into powder and weighed. AR grade solvent were used in this experiment.

B. HPLC Analysis

HPLC analysis was carried out by Shimadzu LC-10AD VP instrument equipped with a C18 column. The injection volume was 20 μl for both samples and catechin and epicatechin hydrate standards (Sigma) with a flow rate of 1 μl / min. The mobile phase used was water:acetonitrile:methanol in different ratios (83:6:11, v/v/v) and the samples were dissolved in 40% acetone. Detection was carried out at 280 nm for catechin and epicatechin standards at ambient temperature. The samples were injected 3 times to confirm the retention time of the identified peak. External standards of catechin and epicatechin hydrates (10-100 mg/l) were freshly prepared to generate a calibration curve.

C. Specimen preparation

The mild steel (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. Mild steel 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 cm^2 were used for the electrochemical studies.

D. Weight Loss Measurements

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 \pm 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^[4]:

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

Where,

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

E. 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^[4]:

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

Where, $R_{\text{ct}(o)}$ and $R_{\text{ct}(i)}$ 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^[4].

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

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

F. Scanning Electron Microscope (SEM)

The surface morphology of steels specimens were evaluated by SEM analysis (Leo Supra 50VP). A test specimen that exhibit higher efficiency of corrosion inhibition from weight loss measurement was examined with scanning electron microscopy (SEM) instead of blank (without inhibitor) and fresh steel.

III. RESULTS AND DISCUSSION

A. HPLC Analysis

The identification of phenolic compounds were carried out using HPLC analysis. Attention was focused on catechin and epicatechin as a phenolic compounds which is a polar molecule (Figure 1). Based on a previous study, The HPLC conditions were: isocratic elution using mobile phase composition of water:acetonitrile:methanol (83:6:11); flow rate, 1 mL min⁻¹; monitored at 280 nm. Under these conditions, all the analytes were separated in less than 7 min.

B. Weight Loss Measurements

The % IE obtained for different concentrations of green tea extract is showed in Table 1. The results prove a positive correlation between the concentration of gambir 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 gambir extract concentration, thus the mild steel surface is efficiently blocked from the hydrochloric acid. The maximum % IE was obtained at maximum concentration of 150 mg L⁻¹ for gambir extracts and was found to be 76.52..

C. Electrochemical method (Potentiodynamic Polarization Measurements)

Figure 3 represents the anodic and cathodic polarization curve of mild steel in different

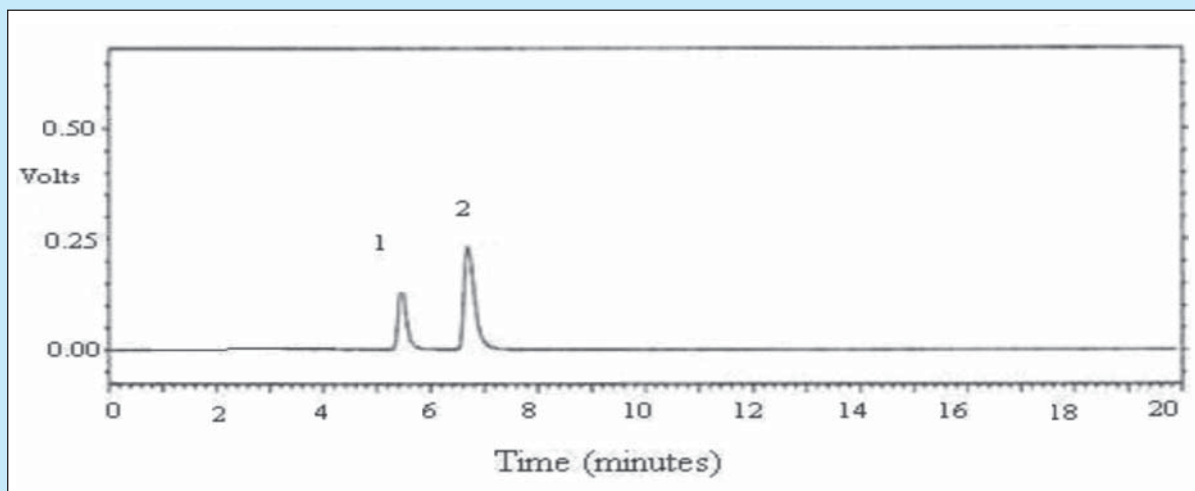


Figure 1
Typical chromatograms for the separation of catechins (1) and epicatechin (2) in Gambir extract using monolithic column

concentrations of acidic solutions of gambir extract. By extrapolating the Tafel anodic and cathodic linear parts until they intersect as straight lines and show the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) as well as resistance polarization (R_p). A steady state of corrosion current density (i_{corr}) occurs when the measured curve becomes horizontal^[9]. Basically, anodic polarization is the shift of anode potential to the positive (noble) direction whereas cathodic polarization is the shift of cathode potential to the negative (active) direction. A study of corrosion prevention and protection have supported that mixed type of inhibitors are generally represented by organic compounds with donor atoms Se, S, N or O instead of having reactive functional groups which latch on to the metal^[10]. For this reason, it was confirmed by potentiodynamic polarization curve that gambir extract exhibits a anodic inhibitor. Electrochemical corrosion parameters obtained from the Tafel analysis of the polarization curve from Figure 2 were illustrated in Table 2.

D. Electrochemical impedance spectroscopy (EIS)

EIS analysis shows typical Nyquist plots for gambir extract which are given in Figures 3.

It is also observed from Table 3 that the R_{ct} values increased with increasing concentrations of

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

Inhibitor	Concentration	Weight Loss	% IE
-	0	0.0558	
Gambir extract	10	0.0345	38.17
	50	0.0267	52.15
	100	0.0184	67.02
	150	0.0131	76.52
	200	0.0150	73.12

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^[11]. The % IE of impedance results, are in good agreement with the polarisation and weight loss studies that shows maximum of

88.28% for gambir extracts for the maximum concentration of 150 g mL⁻¹.

E. SEM Studies

To monitor the morphological changes on the mild steel surface during the corrosion process, SEM

– EDX studies were carried out. Mild steel specimens were screened after the potentiodynamic polarisation studies and the micrographs are given in Figures 5. It was observed that the surface of mild steel is very rough and severely damaged in absence of inhibitor while in Figure 5B the surface is transformed into

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

Conc. (ppm)	E(i=0), mV	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Ba (mV/dec)	-Bc (mV/dec)	IE (%)
0	-503	3.1327	315.7	339.8	-
10	-437	1.8123	213.9	221.8	42.15
50	-308	0.9799	204.7	220.5	68.72
100	-191	0.7831	251.4	270.4	75.00
150	-161	0.3670	261.3	181.1	88.28
200	-179	0.6399	291.8	250.6	79.57

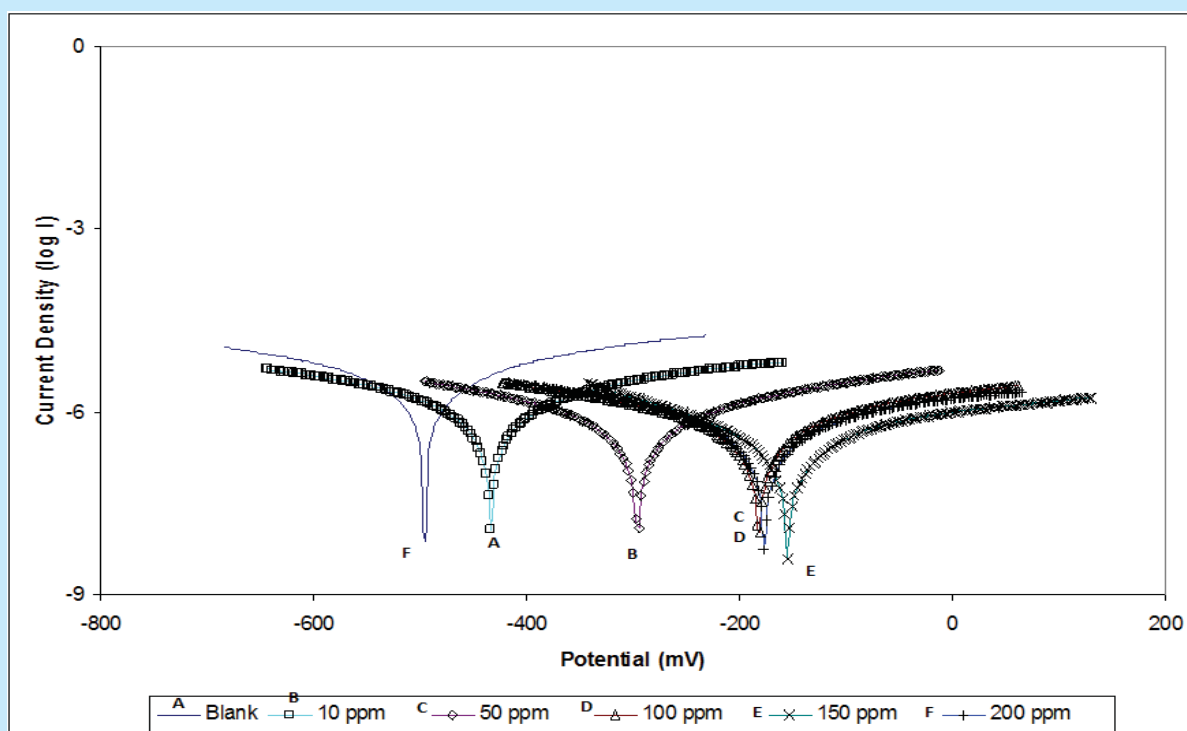


Figure 2
Tafel plots of gambir extracts on mild steel in 1.0 M HCl

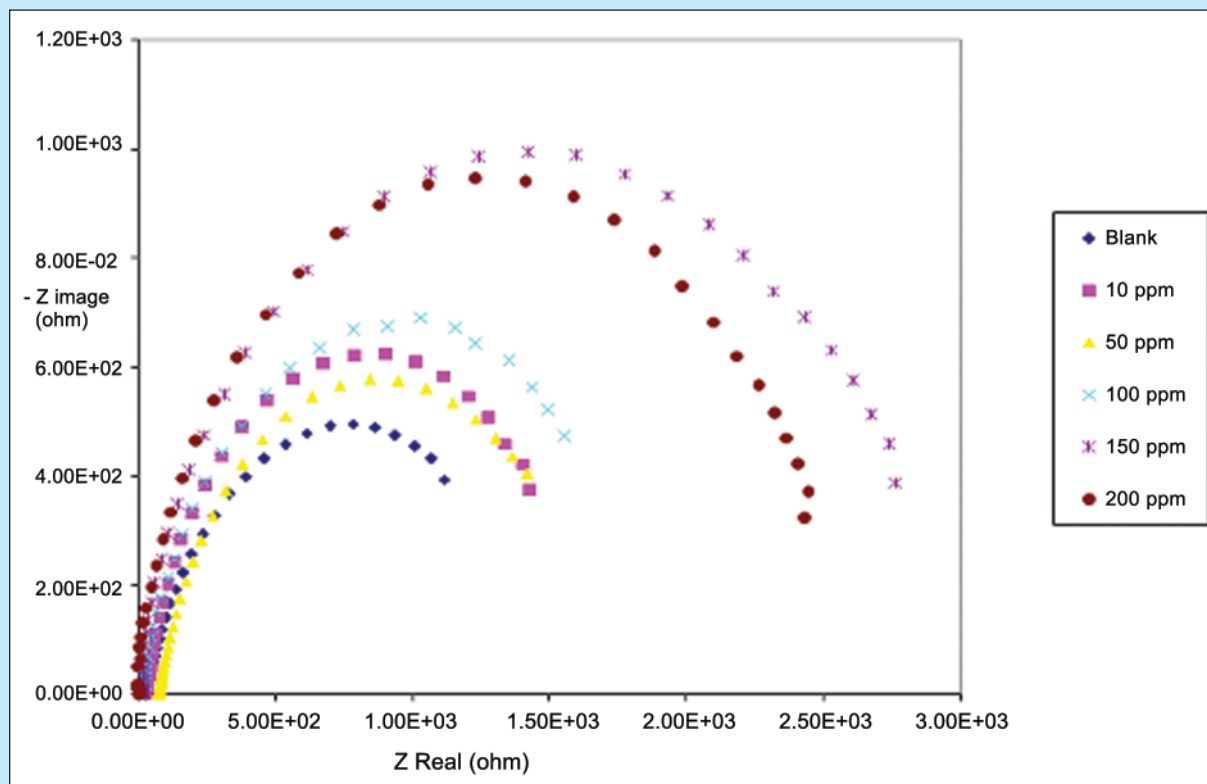


Figure 3
Nyquist plots of gambir extract on mild steel in 1 M HCl

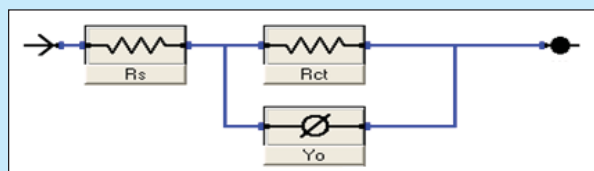


Figure 4
The Randles CPE circuit which is the equivalent circuit for this impedance spectra

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

Conc. (ppm)	R_{ct} (ohms) $\times 10^3$	R_s (ohms)	% IE
0	1.471	37.65	0
10	1.628	67.59	44.29
50	1.582	78.52	52.05
100	1.755	87.56	57.00
150	2.494	111.62	66.27
200	2.135	96.16	60.85

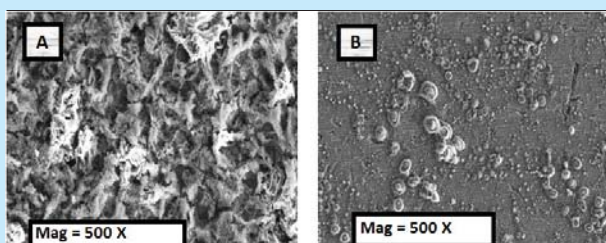


Figure 5
SEM images of mild steel in 1M HCl medium
(A) absence of inhibitor
(B) presence of gambir extract

smoother, more uniform deposit with cracks upon addition of gambir extract.

IV. CONCLUSION

Gambir extract are good inhibitors for mild steel in 1 M HCl. The inhibition efficiency obtained via electrochemical measurements is in good agreement

with that obtained by using the weight loss method. SEM analysis shows that the morphology of inhibited mild steel was improved compared with uninhibited mild steel.

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