

## Electrochemical Studies of Mild Steel Corrosion Inhibition in Aqueous Solution by *Uncaria gambir* Extract

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**Abstract:** The inhibition of the corrosion of mild steel in aqueous solutions by ethyl acetate extract of *Uncaria gambir* containing catechin has been studied using weight loss, potentiodynamic polarisation measurements, electrochemical impedance spectroscopy (EIS) and scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDX). Inhibition was found to be highest at a concentration of 150 ppm in solutions with a pH of 5. The results obtained show that the ethyl acetate extract of *U. gambir* acts as a mixed-type inhibitor and could serve as an effective corrosion inhibitor of mild steel in aqueous solution.

**Keywords:** *Uncaria gambir*, catechin, corrosion inhibitor, weight loss, potentiodynamic polarisation measurement

**Abstrak:** Pemerencatan kakisan besi lembut dalam larutan akueus oleh ekstrak etil asetat *Uncaria gambir* yang mengandungi katekin dalam larutan akueus telah dikaji dengan menggunakan kaedah kehilangan berat, pengukuran potensiodinamik keikutuban, spektroskopi elektrokimia impedans (EIS) dan mikroskop elektron imbasan dengan spektroskopi sinar-X sebaran tenaga (SEM-EDX). Pemerencatan tertinggi dikesan pada kepekatan 150 ppm dalam larutan pH 5. Keputusan yang diperolehi menunjukkan bahawa ekstrak etil asetat *U. gambir* bertindak sebagai perencat jenis campuran dan boleh bertindak sebagai perencat kakisan besi lembut yang efektif dalam larutan akueus.

**Kata kunci:** *Uncaria gambir*, katekin, perencat kakisan, kehilangan berat, pengukuran potensiodinamik keikutuban

### 1. INTRODUCTION

*Uncaria gambir*, a native Southeast Asian herbal plant, can mostly be found in countries such as Indonesia and Malaysia.<sup>1</sup> It had been widely used as an astringent medicine for the treatment of spongy gums, tooth acne, diarrhea and sore throat.<sup>2</sup> Besides being chewed, it is also imported in large quantities by the West for tanning, calico printing and dyeing purposes.<sup>3</sup> Previous studies showed that gambir consists mostly of the flavan monomer, which contains (+)-catechin, (+)-epicatechin and alkaloids.<sup>4</sup> Catechins are flavonoids ( $C_6-C_3-C_6$ ) that are

mostly found in fruits and plants such as tea leaves, wine and potatoes.<sup>5</sup> Interestingly, catechin exhibits an anti-oxidative activity that stops oxidation and corrosion, the deterioration process and discoloration.<sup>6</sup>

Corrosion affects most of the industrial sector and may cost billions of dollars each year for prevention and replacement maintenance.<sup>7</sup> Thus, the modern world has made investigations to overcome this problem by conducting enrichment studies of corrosion inhibitors. Corrosion inhibitors will reduce the rate of either anodic oxidation or cathodic reduction or both. This will give us anodic, cathodic or a mixed type of inhibition. Most of the potential corrosion inhibitors possess an active functional group, such as a nitro (-NO<sub>2</sub>) or a hydroxyl (-OH)<sup>8,9</sup> group.

In an attempt to find corrosion inhibitors that are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in acid cleaning processes. This study was done to evaluate the inhibitive effect of ethyl acetate extract of *U. gambir* as a green corrosion inhibitor of mild steel in aqueous solution. The assessment of the corrosion behaviour was studied using weight loss and potentiodynamic polarisation measurements, and the morphology of inhibited mild steel surface was analysed by scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDX).

## 2. EXPERIMENTAL

### 2.1 Sample Preparation

Gambir samples were obtained from Medan Province, Indonesia. The gambir cubes were grinded into fine powder and sieved with a 50-µm mesh. Initially, 5 g of powdered gambir were dissolved in 80°C distilled water (100 ml). Next, the aqueous extract was shaken at 200 rpm (IKA KS 260, IKA Instruments, Sweden) continuously for 1 hour. The impurities were discarded by vacuum filtration (70 mm), and the mother liquors were partitioned with n-hexane (50 ml × 3, QRéC) for purification purposes. The purified aqueous extract was freeze-dried (Labconco Cooperation, Missouri, USA) for 2 days. As a second partition, the resulting aqueous extract powder (1.0 g) was dissolved in ethyl acetate (50 ml, QRéC). The ethyl acetate extract was concentrated at 45°C under reduced pressure in a rotary evaporator (Heidolph Instruments GmbH@Co. KG, Schwabach, Germany). Then, the concentrated extracts were dried in the oven (50°C) and, finally, the dried extract was grinded into powder.

## 2.2 Electrodes

Weight loss measurements were performed using specimens with a composition (in wt%) of Fe: 0.97, C: 0.14, O: 0.15, and 3 cm × 4 cm × 1 mm in dimension. The specimens were first polished to a mirror finish using 400 and 800 grit emery paper, immersed in methanol and finally washed with double distilled water and dried before being weighed and immersed into the test solution. Polarisation measurements were performed using 6 cm × 4 cm × 1 mm specimens of equal composition. The working electrode (WE) is made of mild steel with an exposing geometrical surface area of 0.785 cm<sup>2</sup> to the electrolyte, platinum gauze as the auxiliary electrode (CE), and saturated calomel electrode (SCE) as the reference electrode (RE). Prior to each measurement, the electrode surface was pretreated in the same manner as the weight loss experiments. All experiments were carried out using aerated unstirred solutions at 298 K.

## 2.3 Weight Loss Measurement

### 2.3.1 Effect of concentrations

Specimens in duplicate were immersed for a period of 7 days in 100 ml, pH 5 aqueous solutions containing various concentrations of the studied inhibitors. The mass of the specimens before and after immersion was determined using an analytical balance of 0.001 mg accuracy. Averages of the duplicate values were used. Inhibition efficiencies (gWL) were calculated from the relation:

$$gWL (\%) = \frac{w - w_0}{w} \times 100 \quad (1)$$

where  $w$  and  $w_0$  are the uninhibited and inhibited corrosion rates, respectively.

### 2.3.2 Effect of pH

The same procedures were repeated as above in which the specimens were immersed in 100 ml of various pH (1, 3, 5, 7 and 9) solutions of the inhibitors.

## 2.4 Potentiodynamic Polarisation Measurement

Polarisation measurements were conducted in a conventional 3 electrode Pyrex cell with an overall volume of 300 cm<sup>3</sup>. A platinum gauze and SCE were used as the CE and the RE, respectively. Measurements were carried out using a PC controlled Volta Lab PGP 201 system with Voltamaster 4 software

(Radiometer Analytical SAS, Villeurbanne Cedex, France). The potentials were scanned at a scan rate of  $1 \text{ mVs}^{-1}$  from the corrosion potential ( $E_{\text{corr}}$ ) in the cathodic direction and, subsequently, in the anodic direction. The electrode was held in the test environment for 30 min prior to each experiment, which provided sufficient time for  $E_{\text{corr}}$  to attain a reliable stable value. Inhibition efficiencies, (nPol), were calculated using the relation:

$$\text{nPol (\%)} = \frac{i - i_0}{i} \times 100 \quad (2)$$

where  $i$  and  $i_0$  are the uninhibited and inhibited corrosion current densities, respectively.

## 2.5 Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy, EIS, was carried out with the open circuit potential,  $E_{\text{oep}}$ , for every sample; all of the samples were immersed for 60 min over a frequency range of 100 kHz–1 Hz with a signal amplitude perturbation of 5 mV and a scan rate of  $1 \text{ mVs}^{-1}$ . Next, it was fitted with sets of circuits that give the best value. The inhibition efficiency, IE, was calculated by the following equation:

$$\text{IE (\%)} = \{1 - (R_{\text{ct}}/R'_{\text{ct}})\} \quad (3)$$

where  $R_{\text{ct}}$  and  $R'_{\text{ct}}$  refer to charge transfer resistance without and with the addition of an inhibitor (ethyl acetate extract of gambir), respectively. The Nyquist plot was calculated using Echem Analyst software (Gamry Instrument, Warminster, PA, USA).

## 2.6 Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The surface morphology of the mild steel specimen was evaluated by SEM-EDX analysis with Leo Supra 50 VP (Carl-Zeiss SMT, Oberkochen, Germany) and Oxford INCA400 (Oxford Instrument Analytical, Bucks, UK). The specimen that shows high inhibition was examined with specimens without inhibitors and fresh steel.

### 3. RESULTS AND DISCUSSION

#### 3.1 Weight Loss Measurement

Using the experimental weight loss data, the percentage of gWL, was calculated in the classical way. The value of gWL for all investigated concentrations and pHs of ethyl acetate gambir extract are summarised in Tables 1 and 2, respectively. Based on the results, it is shown that the inhibitor is concentration-independent as the concentration starts to decrease at 200 ppm (Fig. 1). Thus, this means that the highest inhibition is at 150 ppm in pH 5 (Fig. 2). Interestingly, the colour changes of our electrolyte were observed and showed a yellowish colour of ferrous or ferric hydroxide at the concentration of 0 ppm and 10 ppm. The colour changes of dark blue magnetite were observed for the rest of the concentrations. This means that the protective film of a stable oxide of magnetite was formed on the mild steel. Magnetite will strongly adhere to the metal and consequently results in an impermeable layer being formed to stop further corrosion.<sup>10,11</sup>

Table 1: Inhibition efficiencies for various concentration of ethyl acetate extract of *U. gambir* for the corrosion of mild steel in pH 5 aqueous solution.

| Conc. (ppm) | Weight before (g) | Weight after (g) | Weight loss (g) | gWL (%) |
|-------------|-------------------|------------------|-----------------|---------|
| 0           | 4.3201            | 4.2927           | 0.0274          | —       |
| 10          | 4.4103            | 4.3914           | 0.0189          | 31.02   |
| 50          | 4.5139            | 4.4982           | 0.0157          | 42.70   |
| 100         | 4.3132            | 4.3012           | 0.0120          | 56.20   |
| 150         | 4.4394            | 4.4306           | 0.0088          | 67.88   |
| 200         | 4.4305            | 4.4210           | 0.0095          | 65.32   |

Table 2: Inhibition efficiencies for various pH of 150 ppm ethyl acetate extract of *U. gambir* for the corrosion of mild steel in aqueous solution.

| pH | Weight before (g) | Weight after (g) | Weight loss (g) | gWL (%) |
|----|-------------------|------------------|-----------------|---------|
| 1  | B: 4.5993         | 4.5251           | 0.0742          | —       |
|    | S: 4.5078         | 4.4428           | 0.0650          | 12.39   |
| 3  | B: 4.8150         | 4.7842           | 0.0308          | —       |
|    | S: 4.7849         | 4.7677           | 0.0172          | 44.16   |
| 5  | B: 4.3201         | 4.2927           | 0.0274          | —       |
|    | S: 4.4394         | 4.4306           | 0.0088          | 67.88   |
| 7  | B: 4.6183         | 4.5955           | 0.0228          | —       |
|    | S: 4.5058         | 4.4935           | 0.0150          | 34.21   |
| 9  | B: 4.6034         | 4.5808           | 0.0226          | —       |
|    | S: 4.5196         | 4.5001           | 0.0195          | 13.71   |

Note: B: blank, S: 150 ppm extract

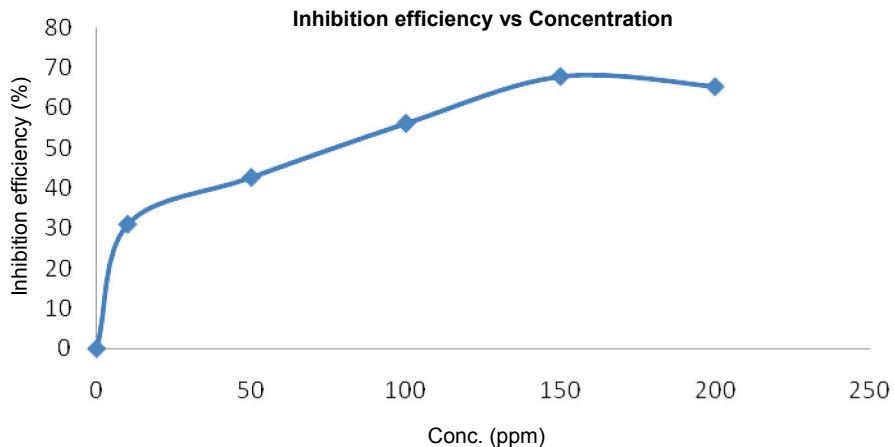


Figure 1: The relation between percentage of inhibition with concentration of ethyl acetate extract of *U. gambir*.

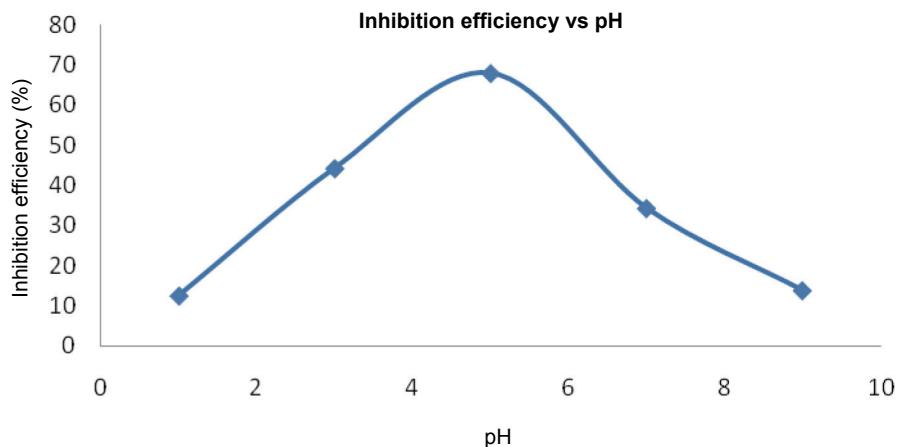


Figure 2: The relation between percentage of inhibition with pH of ethyl acetate extract of *U. gambir*.

### 3.2 Potentiodynamic Polarisation Measurement

The evaluation of nPol can also be performed through electrochemical experiments, which consist of the determination of Tafel curves. Tafel plots of mild steel in pH 5 aqueous solutions with and without inhibitors for various concentrations were summarised in Figure 3 and Table 3, whereas the corrosion potential and the various kinetic data for all pH range were summarised in Table 4. It should be noted that, with the addition of the compound, both the anodic and cathodic current densities decrease, with the anodic domain being more

significant. Although the marked positive shift (noble values) in the corrosion potential, and the decrease in the anodic current density in the presence of the inhibitor, suggests that these compounds act as an anodic-type inhibitor, there is also a decrease in the cathodic current density, which indicates that these compounds act as mixed-type inhibitors. In a nutshell, this test supports the fact that the concentration of 150 ppm at pH 5 will give the best inhibition.

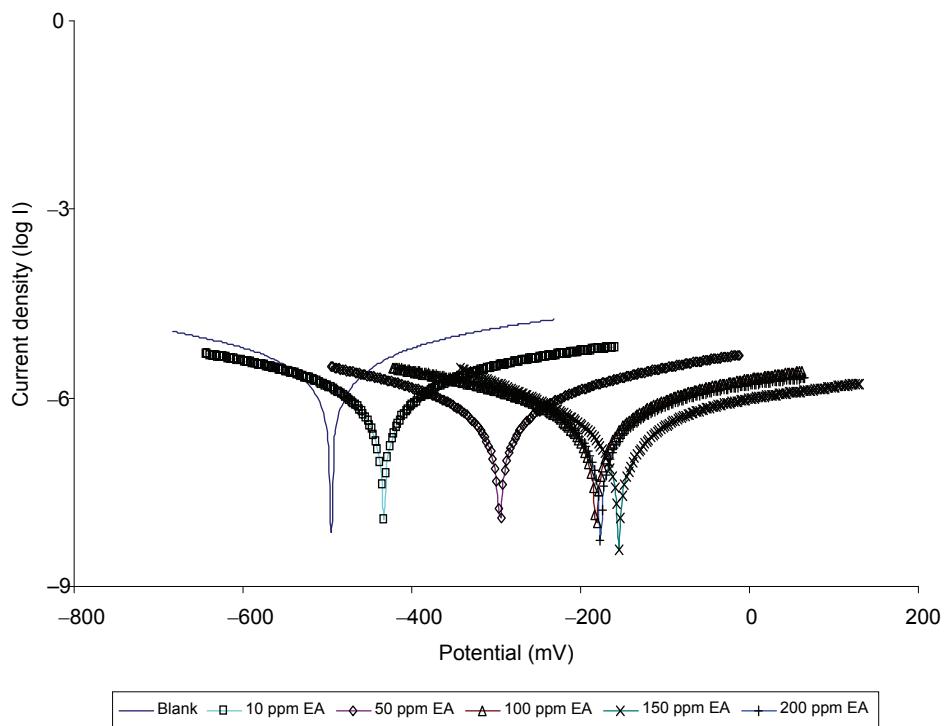


Figure 3: Polarisation curve for mild steel in pH 5 aqueous solutions with absence and presence of various concentration of ethyl acetate extract of *U. gambir*.

Table 3: Corrosion parameters for mild steel in pH 5 aqueous solution with absence and presence of various concentration of ethyl acetate extract of *U. gambir*.

| Conc.<br>(ppm) | E (i = 0),<br>mV | I <sub>corr</sub><br>( $\mu\text{A}/\text{cm}^2$ ) | R <sub>p</sub><br>( $\text{k}\Omega\cdot\text{cm}^2$ ) | B <sub>a</sub><br>(mV) | -B <sub>c</sub><br>(mV) | Corr,<br>m/Y | IE (%),<br>I <sub>corr</sub> |
|----------------|------------------|--|--|------------------------|-------------------------|--------------|------------------------------|
| 0              | -502             | 3.2472   | 16.21  | 314.2                  | 342.3                   | 37.98        | —                            |
| 10             | -439             | 0.8085   | 43.53  | 211.5                  | 222.5                   | 9.456        | 75.10                        |
| 50             | -302             | 0.4833   | 75.29  | 205.4                  | 219.6                   | 5.652        | 85.12                        |
| 100            | -188             | 0.4616   | 94.19  | 258.2                  | 265.3                   | 5.398        | 85.78                        |
| 150            | -159             | 0.2664   | 145.74   | 259.6                  | 179.3                   | 3.115        | 91.79                        |
| 200            | -181             | 0.4400   | 100.73   | 289.1                  | 248.1                   | 5.146        | 86.45                        |

Table 4: Corrosion parameters for mild steel in aqueous solution with absence and presence of various pH of 150 ppm ethyl acetate extracts of *U. gambir*.

| pH | E(i = 0) | $i_{corr}$<br>( $\mu\text{A}/\text{cm}^2$ ) | Rp<br>( $\text{k}\Omega\cdot\text{cm}^2$ ) | Ba<br>(mV) | -Bc<br>(mV) | IE<br>(%) |
|----|----------|---|--|------------|-------------|-----------|
| 1  | -554     | 89.1  | 0.2657                                     | 89.5       | 198.1       | —         |
|    | -552     | 105.3                                       | 0.2971                                     | 101.7      | 235.0       | -18.18    |
| 3  | -673     | 26.1446                                     | 1.66                                       | 366.4      | 350.1       | —         |
|    | -631     | 24.2667                                     | 2.02                                       | 401.4      | 496.0       | 7.18      |
| 5  | -502     | 3.2472                                      | 16.21                                      | 314.2      | 342.3       | —         |
|    | -159     | 0.2664                                      | 145.74                                     | 259.6      | 179.3       | 91.77     |
| 7  | -245     | 0.2385                                      | 156.50                                     | 241.3      | 198.6       | —         |
|    | -238     | 0.1484                                      | 170.02                                     | 176.5      | 150.8       | 37.77     |
| 9  | -315     | 0.6174                                      | 76.80                                      | 353.3      | 248.2       | —         |
|    | -340     | 1.4338                                      | 27.93                                      | 243.4      | 201.3       | -56.94    |

### 3.3 Electrochemical Impedance Spectroscopy (EIS)

The EIS method is very useful in characterising electrode behaviour. The electrode characterisation includes the determination of the polarisation resistance (Rp), corrosion rate and the electrochemical mechanism. The usefulness of these data permits the analysis of the alternating current (AC) impedance data, which are based on modelling a corrosion process by an electrical circuit. The EIS technique is based on the response of an equivalent circuit for an electrode/solution interface. The response can be analysed by transfer functions due to an applied small-amplitude potential excitation at varying signals and sweep rates. In turn, a sine-wave perturbation of small amplitude is employed on a corroding system being modelled as an equivalent circuit for determining the corrosion mechanism and polarisation resistance.<sup>12</sup> Table 5 lists the impedance parameters of the Nyquist plots of the ethyl acetate extract of gambir in different concentrations. From this experiment, the Nyquist plot shows that, at a concentration of 150 ppm, the percentages of inhibition efficiency are highest when the charge transfer potential,  $R_{ct}$ , is also in good agreement (Fig. 4). In these spectra, the variation of impedance responses of mild steel after the addition of the ethyl acetate extract of gambir to the pH 5 aqueous solution is remarkable. The Randles CPE circuit was known as the equivalent circuit in our study (Fig. 5).

Table 5: Impedance parameters and inhibition efficiency for mild steel in pH 5 aqueous solution containing different concentrations of ethyl acetate extract of gambir.

| Conc.<br>(ppm) | $R_{ct} (\Omega) \times 10^3$ | $R_s (\Omega)$ | $Y_o \times 10^{-6}$ | $N \times 10^{-3}$ | IE<br>(%) |
|----------------|-------------------------------|----------------|----------------------|--------------------|-----------|
| 0              | 1.471                         | 24.39          | 908.9                | 746.8              | 0         |
| 10             | 1.628                         | 26.41          | 669.3                | 829.9              | 9.6       |
| 50             | 1.582                         | 73.43          | 375.7                | 805.9              | 7.01      |
| 100            | 1.755                         | 14.71          | 641.6                | 836.7              | 16.18     |
| 150            | 2.494                         | 13.40          | 289.6                | 909.7              | 41.02     |
| 200            | 2.135                         | 3.231          | 245.7                | 991.4              | 31.1      |

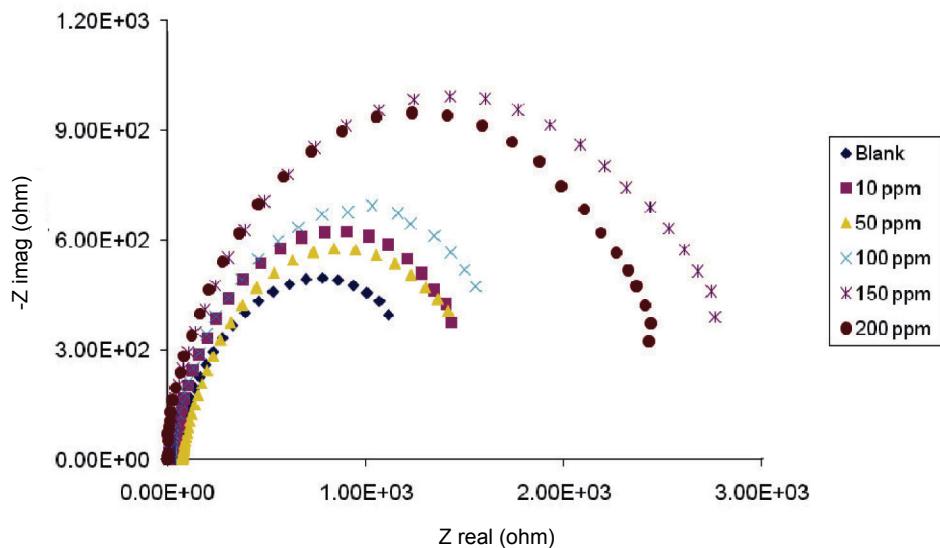


Figure 4: Nyquist plot for mild steel in pH 5 aqueous solution in presence of ethyl acetate extract of gambir.

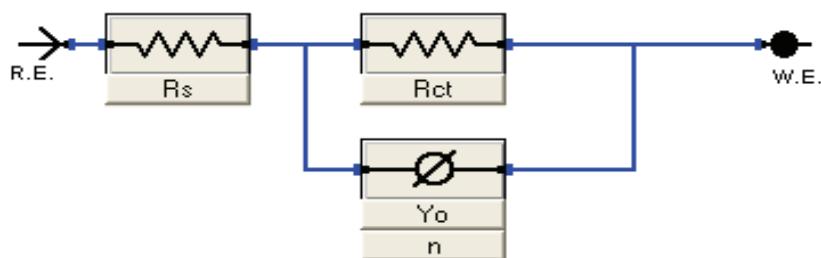
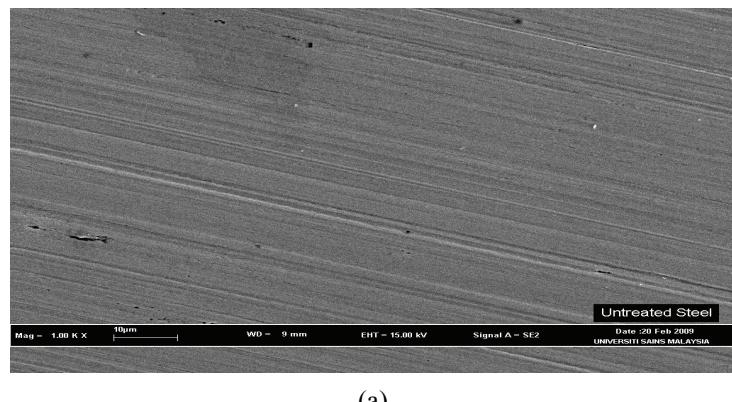


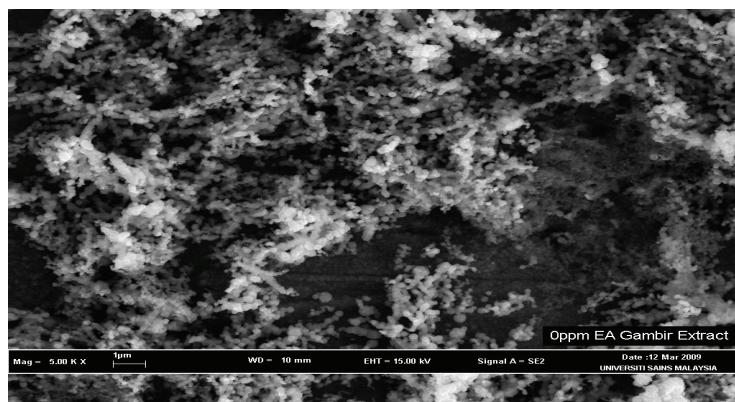
Figure 5: The Randles CPE circuit which is the equivalent circuit for the impedance spectra.

### 3.4 Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Figure 6 shows the SEM micrographs of different slides of mild steel after immersion in the aqueous solution with the absence and presence of the inhibitor. Here, the micrograph exhibited a cocoon-like structure for solution with the absence of the inhibitor. This explains the fact that the surface was already undergoing a localised attack, which resulted in a cocoon-like structure, whereas there was an improvement in the surface morphology of mild steel that was treated with the inhibitor. From the EDX evaluation, it is clear that the upraising value of O is due to the formation of the ferrous hydroxide, whereas, for C, it is due to the presence of catechin that acts as the active inhibitor and complexes with the mild steel surface (Table 6 and Fig. 7).

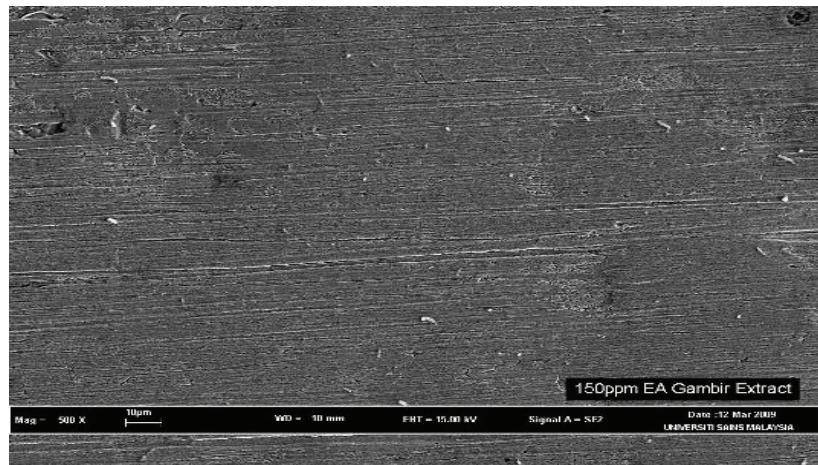


(a)



(b)

Figure 6: SEM micrographs of mild steel in (a) fresh steel, (b) without inhibitor, 0 ppm (c) with inhibitor, 150 ppm (*continued on next page*).

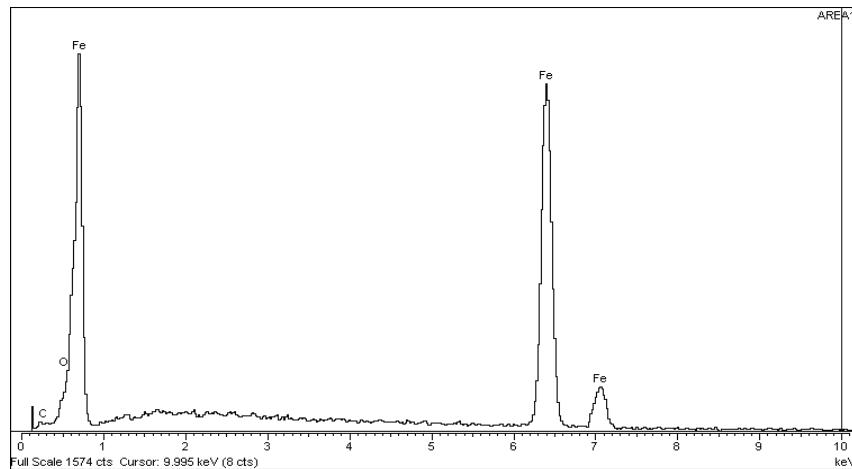


(c)

Figure 6: (continued).

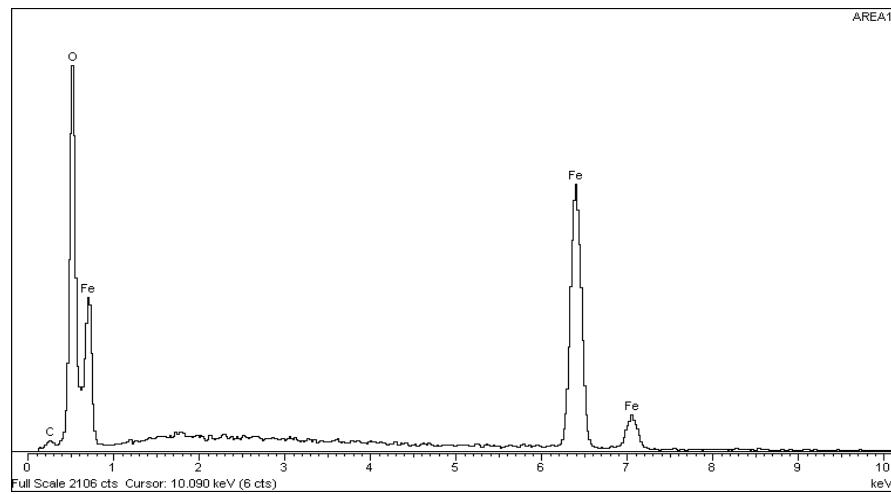
Table 6: The composition of the sample regarding the EDX analysis.

| Sample                       | Element (%) |       |      |
|------------------------------|-------------|-------|------|
|                              | Fe          | O     | C    |
| Fresh mild steel             | 97.02       | 1.54  | 1.44 |
| Mild steel without inhibitor | 74.87       | 23.63 | 1.49 |
| Mild steel with inhibitor    | 96.18       | 1.23  | 2.59 |

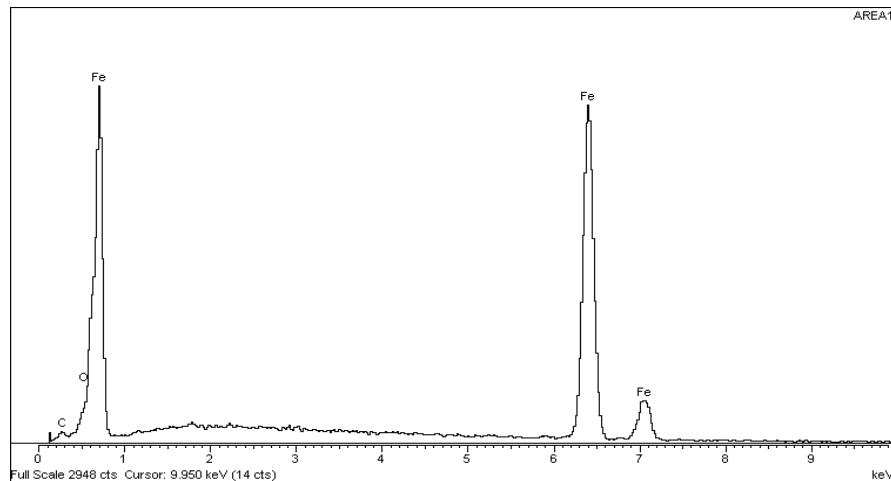


(a)

Figure 7: The EDX spectra of mild steel in (a) fresh steel, (b) without inhibitor, 0 ppm (c) with inhibitor, 150 ppm (continued on next page).



(b)



(c)

Figure 7: (continued).

#### 4. CONCLUSION

The electrochemical studies proved that the ethyl acetate extract of *U. gambir* displays inhibitor properties that work best at a concentration of 150 ppm and at a pH of 5. The polarisation measurement demonstrates that the extract under investigation acts as a mixed-type inhibitor, and the electrochemical impedance spectra shows inhibition when the sample was fitted with the Randles

CPE circuit. SEM-EDX analysis shows that there was some improvement in the surface morphology of inhibited mild steel compared with uninhibited mild steel.

## 5. ACKNOWLEDGEMENT

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