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CORROSION INHIBITION OF MILD STEEL IN ACIDIC SOLUTION BY ETHANOL EXTRACT OF *UNCARIA GAMBIR*

M. Jain Kassim*, W. Jian Ming, M. Hazwan Hussin, T. Kang Wei

Material Chemistry and Corrosion Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800, Penang, Malaysia.

*Email: mjain@usm.my

ABSTRACT

Corrosion inhibition effect of ethanol extract of *Uncaria gambir* on mild steel in 1 M HCl medium has been investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). It was found that the presence of the gambir extract reduces markedly the corrosion rate of mild steel in the acid solution. The corrosion inhibitive effect of gambir extract is concentration dependent. The inhibition efficiency increases as the extract concentration is increased and reaches the optimum inhibition of 98% at 3000 ppm according to the weight loss measurement. The polarization study showed that gambir extract acts as a mixed-type inhibitor with the cathodic type predominates. Randles CPE circuit has been used as the equivalent circuit for the impedance test. The Nyquist plots revealed that on increasing the gambir extract concentration, an increase in charge transfer resistance and decrease in the CPE capacitance would result. Surface analysis (SEM-EDX) was also carried out to establish the corrosion inhibitive property of gambir extract in HCl solution.

Keywords: *Uncaria gambir*, Polarisation, Electrochemical impedence spectroscopy, Corrosion inhibition, Surface analysis.

1. INTRODUCTION

Gambir is known as *Uncaria gambir* scientifically and is found in Asia, Africa, South America. Gambir also known colloquially as Gambier, Cat's claw, and Uña de Gato [1]. *Uncaria gambir* is a species in the genus *Uncaria* found in Indonesia. In Indonesia, gambir is used for chewing with betel as well as used for tanning, and dyeing [2]. Gambir is rich in polyphenolic compounds which are known to have many medicinal properties and are important components of Chinese herbal remedies and certain modern medicines. Besides used as a dyeing agent, gambir also taken as food where people chewing it with Betel nut and Areca nut. Gambir is believed to enhance the excretion of gall juice which is used in the stomach as well as intestine [3]. Gambir is being developed to function as plywood adhesive or particle board. These products still have to compete with other sources of wood adhesives, such as Acacia *mearnsii* bark, wood *Schinopsis balansa*, and *Caesalpinia spinosa* pods skin produced in other countries [3].

Normally, gambir is in the form of dried extract of gambir leaves. It was made by boiling the leaves in water. The extract dissolves in hot water and turns brownish in colour. The leaves are then pressed mechanically to squeeze out the liquid. This liquid is then dried into a semi-solid paste and molded into cubes, which are dried under the sun. Gambier is generally packed in 50 kilogram multilayered packing (PP bags inside and gunny bags outside). This extract contains of many polyphenolic compounds which have a variety of usage. The main component of which also contained in many *Uncaria* members are flavonoids (especially *gambiriin*), catechins (up to 51%), tanner substance (22-50%), and a number of alkaloids (such as derivatives *gambirtannin*)[3].

Flavonoids are most commonly known for their antioxidant activity which is used to prolong the food product life. Flavonoids have attracted the consumers and food manufacturers interest for their medicinal properties, especially their potential role in the prevention of cancers and cardiovascular disease. Catechin is a polyphenolic compound of flavonoid group. Usually, flavonoids can be found in many fruits, tea leaves, wine, potatoes and other vegetables and plants. Flavonoids also play an important role in plant protection against pathogens and reducing risk of coronary heart disease and growth of cancer cells in human body [4]. The antioxidant activity of polyphenolic is attributed to free radical scavenging activity, which is determined by their reactivity as hydrogen- or electron donating agents, the stability of the resulting antioxidant-derived radical, their reactivity with other antioxidants and their metal chelation properties [5].

The key structure that polyphenolic compounds that lead to the inhibition properties of gambir extract towards corrosion is the hydroxyl group of phenol which will react to quinines. For those compounds which have hydroxyl group attached to the *ortho*-position of the aromatic ring are allowed to react to quinines.

Acids are corrosive to metals but still widely used in industries and household for many purposes such as pickling, cleaning, removing of rust, catalysis, salts production, etc. Due to the corrosiveness of acids, inhibitors are used to reduce the rate of dissolution of metals to forms salts. Compounds containing nitrogen, sulphur and oxygen have been reported as inhibitors [6]. The principle of corrosion inhibition is based on the absorption and desorption of water by an organic corrosion inhibitor on the surfaces of the metal. The ability of the organic compound to exchange the adsorbed water molecules on the metal surfaces determine the efficiency of that compound to acts as corrosion inhibitor as shown in Figure 1.

There are several criteria that affect the adsorption of the green inhibitor on the surfaces of the metal. These are the electronic structure of inhibiting molecules, steric factor, aromaticity, and electron density at donor site of the inhibitor, the presence of other functional group, the structure of the inhibitor, molecular area and molecular weight of the inhibitor molecule [7.8].

The performance of gambir inhibitors, which is extracted by using 50 % ethanol to retarding the corrosion rate in mild steel, can be determined by several general tests. The potential of corrosion inhibition effects of gambir extract concentration can be determined by potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss measurements. Also, the results obtained from the techniques utilized in this study were compared with the aim of developing a methodology for quickly ascertaining the performance of inhibitors.

2. EXPERIMENTAL

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The corrosion inhibition study was done in three tests which are Electrochemical Impedance Spectroscopy (EIS), potentiodynamic polarization (VoltaLab PGP201) and weight loss measurement.

2.1 *Raw materials*

The raw gambir paste was obtained from Medan, Indonesia. The gambir was molded in tube in shape with brownish color and porous structure. It was mashed in smaller size for easier extracting process.

2.2 *Apparatus*

Potentiodynamic polarization study was carried out using the VoltaLab PGP201 with voltamaster software. Electrochemical Impedance Spectroscopy was run under the using of Gamry. All the analysis for corrosion inhibition studies were performed using 100 % mild steel specimens which are rectangular in shape with dimension 3 cm× 2 cm.

2.3 *Extraction*

The fine raw gambir powder was defatted with n-hexane by soxhlet extraction for 24 hours. The defatted gambir was dissolved in the 50 % aqueous ethanol and macerated for 3 hours for extraction. Suction filtered the extract and dried in the sintered glass in oven at the temperature of 60˚C.

2.4 *Corrosion inhibition measurement*

2.4.1 Weight loss measurement

The weight loss experiments were carried out with metal coupons immersed in 50 mL of 1 M HCl solutions in the absence and in the presence of 50, 100, 500, 1000, and 3000 ppm of gambir extract. The mild steel plate of 3 cm in length and 4 cm in width was pre-cleaned by abraded with grade 400 emery papers followed by grade 600. The plates were washed with distilled water and isopropyl alcohol, dried and then weighed. The specimens were dipped into the acid, taken out, washed, dried and weighed accurately after 24 hours immersions.

2.4.2 Potentiodynamic polarization analysis

A double-walled glass three-electrode cell was used to carry out the corrosion tests. The working electrode was a disc of mild steel with a geometric area of 0.789 cm^2. Prior to each polarization experiment, the electrode surface was polished with 400 emery paper followed by 600 emery paper, cleaned ultrasonically, degreased with IPA, rinsed with deionized water and air-dried. The auxiliary electrode was a platinum net and the reference electrode was a saturated calomel electrode (SCE) connected to the cell by a bridge and a Luggin–Habber capillary. All potentials in the text are quoted versus this reference electrode.

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Briefly, the OCP was measured for 0.5 hour using VoltaLab Potentiostat (Model PGP201) before starting the potentiodynamic polarization experiments. The initial and final potentials were fixed according to the technique employed (Tafel, polarization resistance, etc.). For linear polarization resistance measurement, the potential of the electrode was scanned from −250 mV to +250 mV vs corrosion potential a scan rate of 1.0 mVs^{-1} . The polarization resistance was measured from the slope of *E* vs *i* curve in the vicinity of corrosion potential.

2.4.3 Electrochemical impedance spectroscopy (EIS)

EIS experiments were conducted using computer controlled Gamry electrochemical system. EIS software was used for collecting and evaluating the experimental data. Various equivalent circuit models were fitted to the impedance data using a non-linear optimization compound programme. The electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 30 minutes before the EIS experiment start.

2.4.4 SEM & EDX investigation

The steel specimens which undergo the weight loss analysis are observed under the SEM (Leo Supra 50VP) to see the morphology of its surface and EDX (Oxford INCA 400) to determine its composition. The specimens tested are steel plates immersed in 1 M HCl solution in the absence and presence of inhibitor.

3. RESULTS AND DISCUSSION

3.1 *CORROSION INHIBITION STUDY*

3.1.1 Weight loss measurement

The weight loss results regarding the corrosion parameters for mild steel in 1 M HCl medium in the absence and presence of different concentrations of inhibitors are summarized in Table 1. The corrosion rate, *CR* ($g.day^{-1}.cm^{-2}$) for the studied specimen is determined by using the relation:

$$CR=\frac{W_1-W_2}{A.t} \qquad (1)$$

where W_1 is the weight of the specimen before corrosion, W_2 is the weight of the specimen after corrosion, *A* is the surface area of the specimen and t is the immersion time. The percentage of inhibition efficiency was calculated by using the following equation:

$$\%\ IE=\frac{CR_0-CR}{CR_0}\times 100 \qquad (2)$$

where CR_0 and *CR* are the corrosion rates of mild steel in the absence and presence of the inhibitors, respectively. It can be observed that IE increases with increasing the concentrations until the optimum efficient concentration reached. The results obtained from

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the weight loss measurements are in good agreement with those obtained from the EIS and the polarization methods. The result is represented in the graph in Figure 2.

3.1.2 Potentiodynamic polarization analysis

The effect of gambir extract concentration on the anodic and cathodic polarization behavior of mild steel in 1 M HCl solution has been studied by polarization measurements and the recorded Tafel plots are shown in Figure 3. The respective kinetic parameters derived from the above plots are given in Table 2. The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship:

$$\% \, I.E = \frac{icorr^{0} - icorr}{icorr^{0}} \times 100\% \qquad (3)$$

where i_{corr}^{0} is the corrosion currents in absence of inhibitor, i_{corr} is the corrosion currents in absence of inhibitor. From the measured polarization resistance value, the inhibition efficiency has been calculated using the relationship:

$$\% \, IE = \frac{Rp - Rp_0}{Rp} \times 100 \qquad (4)$$

where R_{p0} and R_p are the polarization resistances in absence and presence of inhibitor respectively.

It is illustrated from the data of Table 2 that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of gambir extract to 1 M HCl solution. The inhibition of this reaction was more pronounced on increasing gambir extract concentration.

From Figure 3, in presence of gambir extract, the corrosion potential of mild steel shifted -1 to 20 mV cathodically compared to the solution without inhibitor and also small change in Tafel slopes were noticed. An inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank [9]. This indicates that gambir extract acts as mixed-type inhibitor with predominant cathodic effectiveness. The cathodic current-potential curves gave rise to parallel lines indicating that the addition of gambir extract to the 1 M HCl solution did not modify the hydrogen evolution mechanism and the reduction of H^+ ions at the mild steel surface taken place mainly through a charge transfer mechanism. The gambir molecule was first adsorbed on the mild steel surface and blocked the reaction sites of the mild steel surface. In this way, the surface area available for H^+ ions was decreased while the actual reaction mechanism remains unaffected [10]. A higher coverage of the gambir extract on the surface was obtained in solutions with the higher concentrations.

3.1.3 Electrochemical impedance sprectroscopy

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In order to obtain information about the kinetics of mild steel corrosion in presence of gambir extracts, the electrochemical process taking place at the open-circuit potential was examined by electrochemical impedance spectroscopy (EIS). EIS measurements of the steel electrode at its open-circuit potential after 30 minutes of immersion in 1 M HCl solution alone and in the presence of various concentrations of gambir extract were performed. The recorded EIS spectrum for steel in 1 M HCl medium in the absence and presence showed one depressed capacitive loop as shown in Figure 4. The diameter of Nyquist plots increased on increasing the concentration of gambir extract indicating strengthening of the inhibitive film. The Nyquist diagram contains a depressed semicircle with the center under the real axis, such a behavior is characteristic for solid electrode which is attributed to surface roughness and inhomogeneities of the metal electrodes. In these cases, the parallel network polarization resistance is usually a poor approximation especially for system where an efficient inhibitor is used. For the description of a frequency independent phase shift between an applied alternating potential and its current response, a constant phase element (CPE) was used instead of capacitance. The CPE, which is considered a surface irregularity of the electrode, causes a greater depression in Nyquist semicircle diagram [11], where the metal –solution interface acts as a capacitor with irregular surface, If the electrode surface is homogenous and plane, the exponential value (n) becomes equal to 1 and the meta-solution interface acts as a capacitor with a regular surface, i.e. when n=1, CPE= capacitance.

Simulation of Nyquist plots with Randle's model containing CPE instead of capacitance and charge transfer resistance (R_{ct}) showed excellent agreement with experimental data. The main parameters deduced from the analysis of Nyquist diagram for 1 M HCl containing various concentrations of gambir extract are given in Table 3. On increasing gambir extract concentration, the charge transfer resistance (R_{ct}) increased and capacitance (CPE) decreased indicating that the increasing gambir extract concentration decreased corrosion rate. Decrease in the capacitance was caused by reduction in local dielectric constant. This observation suggests that the inhibitor molecules acted by adsorption at the metal/solution interface [12]. The lower value of n for 1 M HCl medium indicated surface inhomogeneity resulted from roughening of metal surface due to corrosion. The percentage inhibition efficiency (%IE) was calculated from;

$$\%\,IE=\frac{R_1-R_2}{R_1}\times 100 \qquad (5)$$

where R_1 and R_2 are charge transfer resistance of steel in inhibited and uninhibited solutions and this is shown in Table 3.

3.1.4 SEM & EDX investigation

Scanning Electron Microscope (SEM) of mild steel surface immersed in 1 M HCl medium in absence and presence of 3000 ppm gambir extract are shown in Figure 5. A rough surface was noticed for mild steel immersed in acid solution without the inhibitor. In case of mild steel immersed in 1 M HCl with 3000 ppm gambir extract, a smooth surface was noticed and this showed that gambir extract inhibits corrosion of mild steel in 1 M HCl solution. The samples also undergo the EDX test to determine the composition of each of it (Figure 6). The compositions of each sample are tabulated in the Table 4 and Table 5. These data shows the percentage of Fe, O and C which indicate the condition of the metal. In the corroded sample, the percentage of oxygen is higher because of the formation of $Fe(OH)_3$ as well as other oxides precipitate. The presence of gambir extract as an inhibitor has reduced the oxygen which indicates the decreasing in corrosion rate. The significant value of oxygen decreased shows the effectiveness of this inhibitor.

4. CONCLUSION

The inhibition efficiency of mild steel in 1 M HCl increases on increasing the concentration of gambir extract. Inhibition efficiency up to 98 % has been achieved for 3000 ppm gambir extract. Polarization studies showed that gambir extract acts as a mixed-type inhibitor without modifying the mechanism of hydrogen evolution. AC impedance plots of mild steel showed that charge transfer resistance increases with increase of gambir extract. Corrosion inhibition potential can be attributed to adsorption which is revealed by SEM studies. The adsorbed species formed insoluble complex compounds upon their interaction with the dissolved iron ions. The corrosion inhibition is primarily due to the presence of polyphenolic compounds such as catechins, flavonoid, etc. All these compounds offer protection through adsorption.

4. ACKNOWLEDGEMENTS

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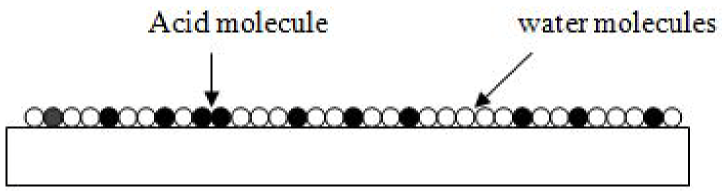
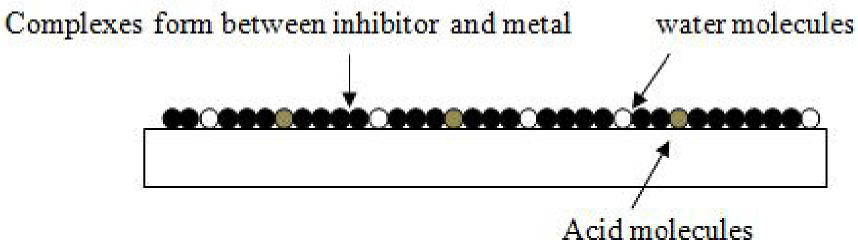
6. FIGURES AND TABLES



(a)



(b)

Figure 1 : The concept of corrosion inhibition of gambir extract on mild steel.(a) without inhibitor (b) with inhibitor.

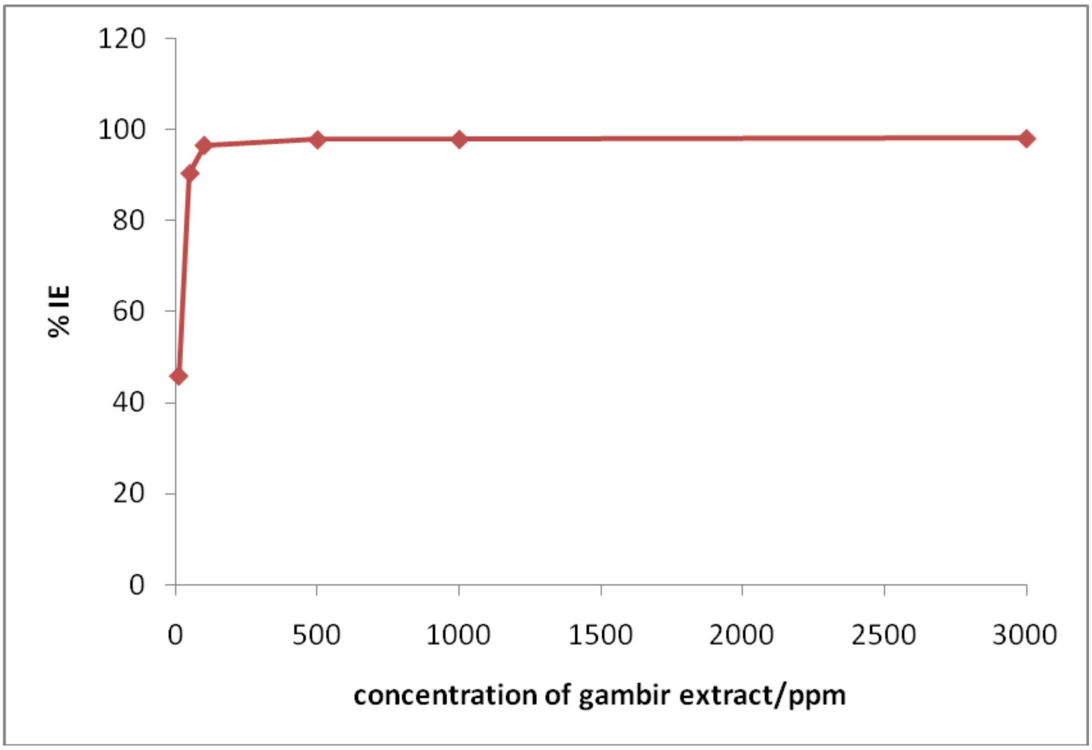


Figure 2: The inhibition efficiency of the presence of gambir extract.

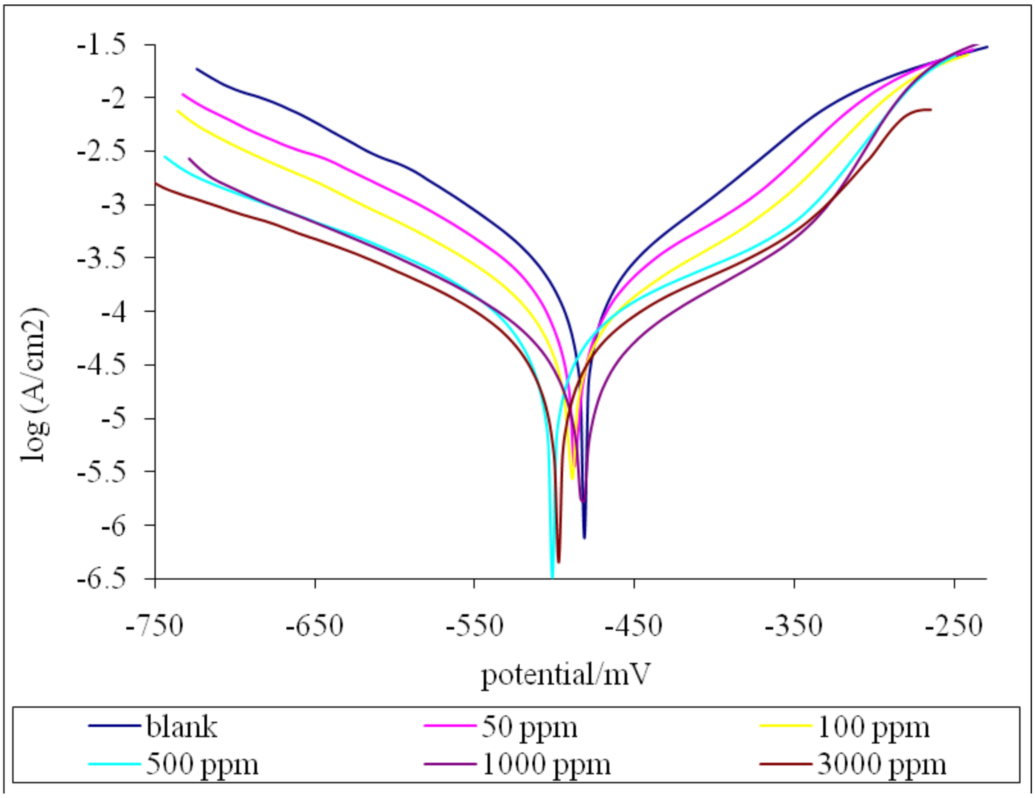


Figure 3: Tafel plot for different concentrations of gambir extract.

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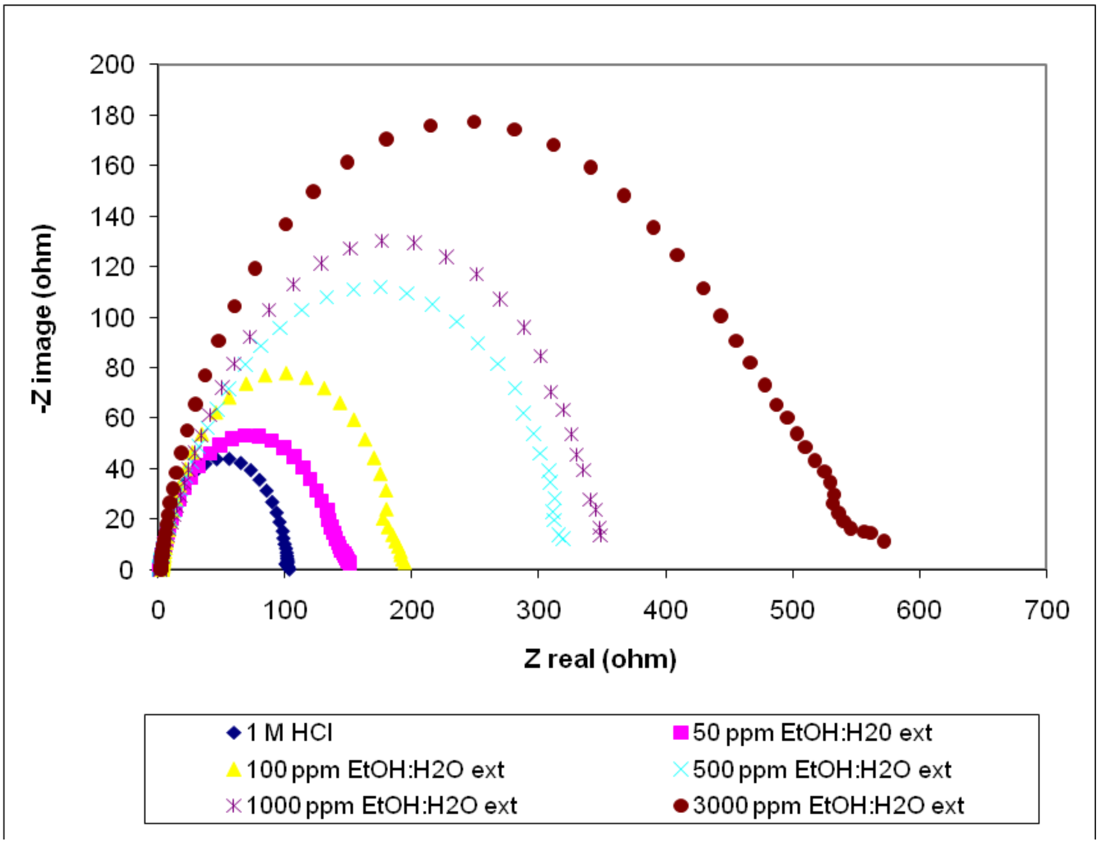
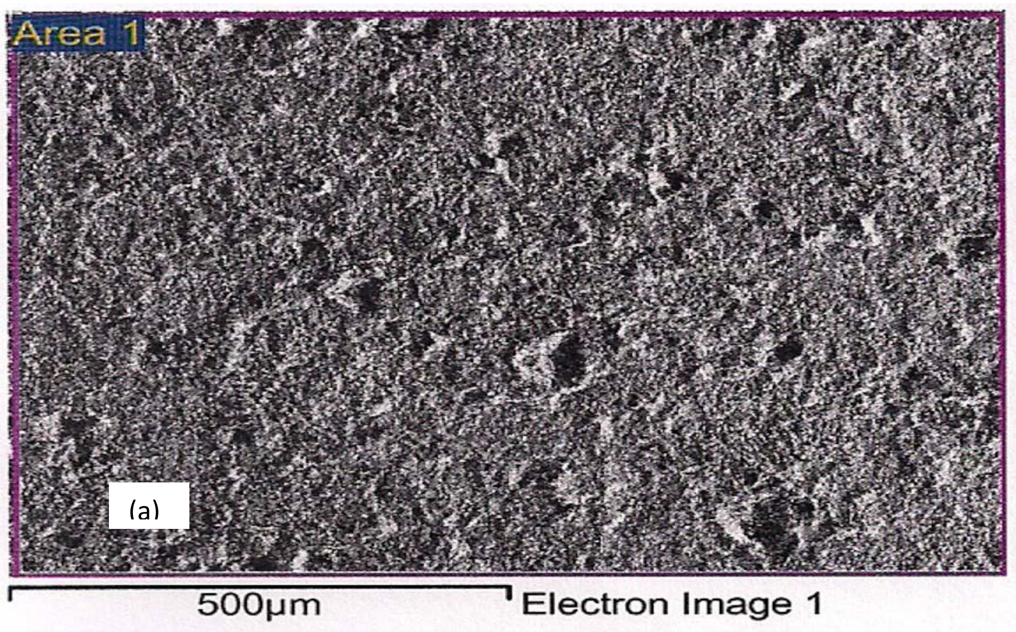


Figure 4: Impedance plots of mild steel in 1 M HCl with and without gambir extract.



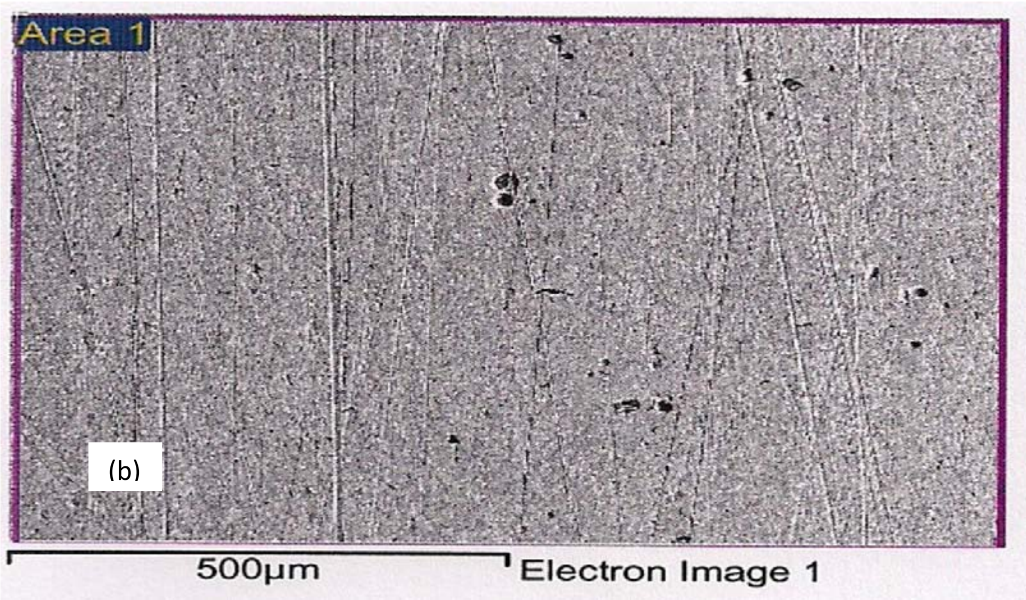
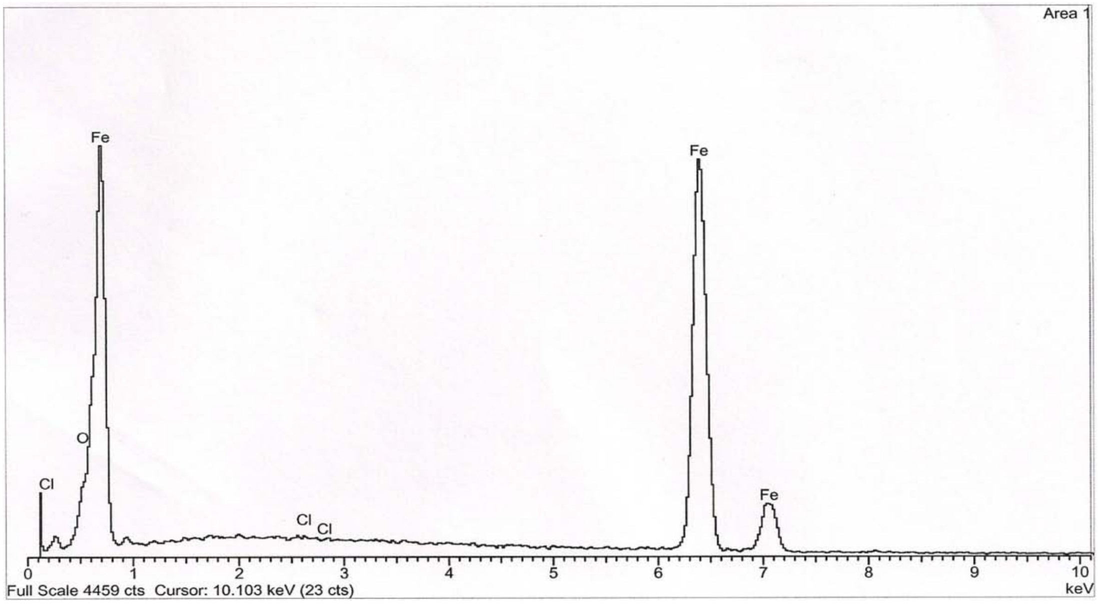


Figure 5: SEM graph of mild steel: (a) mild steel immersed in 1 M HCl and (b) mild steel immersed in 1 M HCl with 3000 ppm of gambir extract.



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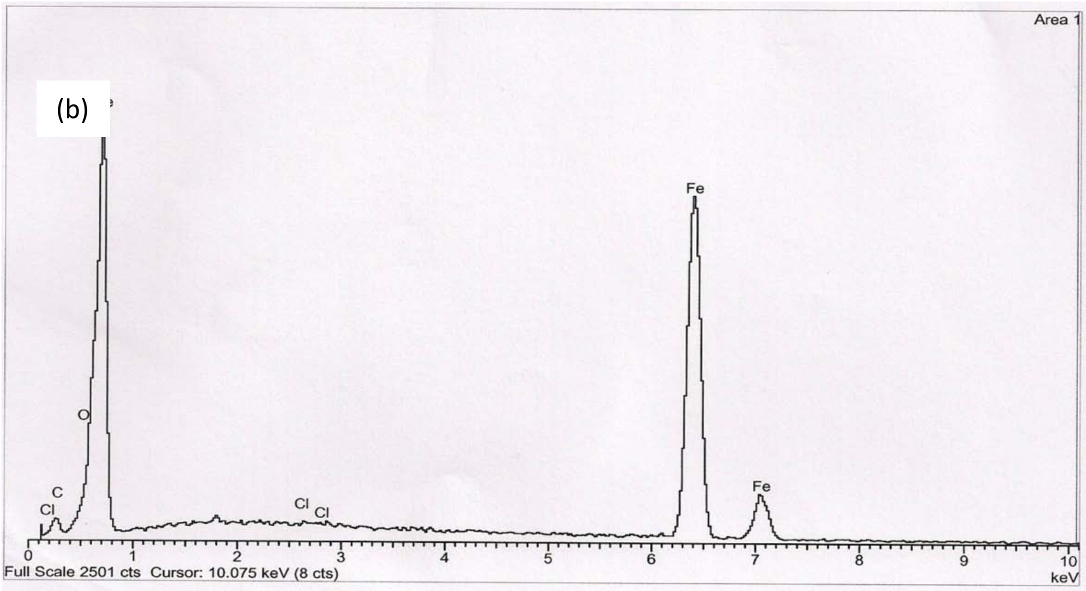

Figure 6: EDX graph of mild steel: (a) mild steel immersed in 1 M HCl and (b) mild steel immersed in 1 M HCl with 3000 ppm of gambir extract.

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Table 1: The corrosion rate and % IE with different concentration of inhibitor

No.	Inhibitor concentration (ppm)	Weight loss (mg)	CR (mmpy)	IE (%)
1	blank	446.5	1.5503	N/A
2	10	245.7	0.8531	44.97
3	50	45.2	0.1569	89.88
4	100	15.3	0.0531	96.57
5	500	9.55	0.0333	97.85
6	1000	9.2	0.0319	97.94
7	3000	8.5	0.0295	98.09

Concentration (ppm)	E_{corr} (mV vs. SCE)	I_{corr} (uAcm^{-2})	b_c (mV/Dec)	b_a (mV/Dec)	corrosion rate (mm/yr)	% inhibition efficiency
0	-488	267.2	-125	102.2	3125.0	N/A
10	-487	246.8	-129.6	111.8	2886.0	7.6
50	-493	190.1	-134.8	105.6	2223.0	28.9
100	-495	111.7	-136.8	100.7	1306.0	58.2
500	-508	110.1	-184.3	105.4	1288.0	58.8
1000	-489	76.7	-103.4	110.9	897.6	71.3
3000	-504	31.3	-190.9	114.7	366.0	88.3

Table 2: Effect of gambir extract on mild steel in 1 M HCl media (Tafel polarization studies)

Table 3: The kinetic parameters derived from Nyquist plots of mild steel immersed in 1 M HCl containing gambir extract.

concentration/ppm	Rct (Ωcm^2)	CPE (μFcm^{-2})	n	I.E (%)
0	79.73	182.6	0.776	N/A
50	112.8	175.5	0.785	29.3
100	148.8	173.4	0.829	46.4
500	250.2	128.9	0.853	68.1
1000	280.3	124.4	0.868	71.6
3000	393.2	60.3	0.905	79.7

Table 4: EDX analysis of the mild steel immersed in 1 M HCl solution without gambir extract inhibitor.

Element	weight %	Atomic %
O K	2.83	9.24
Cl K	0.07	0.10
Fe K	97.10	90.66

Table 5: EDX analysis of the mild steel immersed in 1 M HCl solution with 3000 ppm of gambir extract inhibitor.

Element	weight %	Atomic %
C K	1.80	7.65
O K	1.11	3.55
Cl K	0.11	0.16
Fe K	96.98	88.63