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Corrosion Inhibition of Mild Steel in 2M HCl Using Aqueous Extract of Eggplant Peel

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The objective of this study was to investigate the inhibitive action of eggplant peel extract toward the corrosion of mild steel in 2M HCl solution by employing weight loss measurements and electrochemical techniques. The results of both methods showed that the corrosion rate is decreasing and inhibition efficiency is increasing as the concentration of the eggplant inhibitor increased. The adsorption data were analyzed using various adsorption isotherm models and the results at temperatures of 25, 40 and 50°C have shown that the adsorption behavior of eggplant extract molecules is best described by the Langmuir adsorption isotherm.

Keywords: Adsorption; Corrosion inhibition; Natural inhibitors; Eggplant; Mild-steel

1. INTRODUCTION

Control of internal corrosion of mild steel can be achieved by the injection of corrosion inhibitors. Corrosion inhibitors are surface active compounds that are added in small quantities to stop metal dissolution by a corrosive environment. Vast majority of corrosion inhibitors are made up of molecules which are composed of separate hydrophilic head and hydrophobic tail. Corrosion inhibitions by organic compounds are widely used in industries. Most organic inhibitors control corrosion by adsorption of inhibitor molecules on the metal surface forming thin films. The molecular adsorption depends on the π-electrons and hetero-atoms, such as nitrogen and sulphur, which enhance the adsorption of inhibitor molecules onto the metal surface [1-5]. The use of inhibitors is one the most practical methods for the protection of metals in acidic medias. However, most of organic inhibitors are harmful and toxic to the environment. This has lead to the need for natural products which are eco-friendly and harmless. Several investigators have reported the use of natural inhibitors which were extracted from plant leaves or seeds [6-15].

Natural corrosion inhibitors are mostly obtained from medicinal plants, aromatic spices, and herbs. Plant materials containing phenolic constituents are becoming of great interest to many investigators due to their anti-oxidative activities and nutritional value of food [16-20]. Food-processing generated by-products are rich in phenolic groups that can offer a readily available natural source of anitoxidants [21, 22]. Orange and mango peels extracts were found to provide adequate protection to steel in acidic media [22]. Nandita and Rajini [23] demonstrated that potato peel powder has a considerable antioxidant activity. Matsubara and co-workers [24] showed that nasunin extracted from eggplant peels has antioxidant and antiangiogenic activities. However, little has been done about researching the capabilities of fruit and vegetable peels' extracts as corrosion inhibitors.

In the present study, the inhibition of corrosion of mild steel in 2 M HCl aqueous solution by eggplant peel extract was investigated using weight loss method and electrochemical measurements such as linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and cyclic sweep (CS). The inhibitor active components within eggplant extract were investigated using FT- IR.

2. EXPERIMENTS

2.1 Material

2.1.1 Preparation of eggplant peel stock solution extract

The eggplant peels were heated for two hours in a fluidized bed heater at 80°C, to ensure complete dryness. They were then grinded to fine powder. The eggplant peel extract was prepared by refluxing the eggplant powder in doubled-distilled water for two hours. After the refluxed solution was cooled, it was filtered by vacuum filtration. Concentration of the stock solution was determined by drying a sample and measuring the weight of the residue relative to the volume of the sample taken. Using dilution, stocks with different extract concentrations were prepared.

2.1.2 Specimen preparation

Mild steel C1018 coupons were used in this investigation. The coupons had the composition of (0.18% C; 0.02% Cr; 0.03% Cu; 0.79% Mn; 0.02% Ni; 0.022% P; 0.024% S; 0.21% Si and balance is iron). The coupons had a surface area of 13.63 cm^2 and were used for the weight loss measurements. The specimens were first degreased using ethanol followed by immersion for two minutes in 10% HNO_3 to activate the surface. Afterwards, they were washed using doubled-distilled water followed by rinsing with ethanol. Specimens were dried and then weighed. For the electrochemical tests, 1 cm^2 mild steel specimens were assembled into Teflon specimen holder to represent the working electrode to which electrical connectivity was established. The specimens were first washed using double distilled water, then ethanol, followed by double distilled water, then acetone and finally by double distilled water. Working and reference electrodes were also used to complete the electrochemical setup and generate electrochemical data.

2.2 Methods

2.2.1 Weight Loss Measurements

A pre weighed mild steel specimens with a surface area of 13.63 cm^2 were immersed in 500ml of 2M HCl solution with various extract concentrations ranging from 0 to 1000 ppm. The specimens were left immersed for 7 days in a temperature of 25±2°C. Before taking weight-loss measurements, the metal specimens were washed with doubled-distilled water, immersed in 20% H_2SO_4 for 1 minute, washed thoroughly with water and ethanol, and then dried before reading their weight differences. Inhibition efficiency was calculated using the following relationship

$$\left[IE\% = \frac{W - W_i}{W}\right] * 100 \quad (1)$$

Where W and W_i are corrosion rates of the mild steel without and with eggplant peels extract, respectively.

2.2.2 Electrochemical measurements

A conventional three-electrode cell consisting of a saturated calomel reference electrode, a platinum auxiliary electrode, and the working electrode with 1cm^2 exposed were used. The cell was filled with 600ml of 2M HCl. The Gill AC Potentiostat supplied by ACM Instruments, was used for the electrochemical measurements. Long-term linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and cyclic sweep (CS) tests were performed. The electrochemical tests were performed using various eggplant peel extract concentrations ranging from 0 to 1000 ppm. The settings of each test were as follows: For the LPR test, the start potential was 10 mV, and the finish potential was -10 mV with respect to the open circuit potential. EIS measurements were performed using AC signal amplitude of 20 mV peak to peak in the frequency range of 0.1 Hz to1kHz. The cyclic sweep was recorded at scanning sweep rate of 60mV/min, on a potential range from -150 to 150 mV.

2.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

A Small portion of eggplant peel extract was left to air dry overnight followed by complete drying in a vacuum oven. A KBr pellet was made from the dry extract and was characterized by a Bomem MB-3000 FT-IR equipped with ZnSe optics and a DTGS detector. Spectrum was obtained at 4 cm^{-1} resolution and 200 scans.

3. RESULTS AND DISCUSSION

3.1 Characterization of Eggplant peel Extract

FT-IR spectrum of eggplant peel extract is shown in Figure 1.

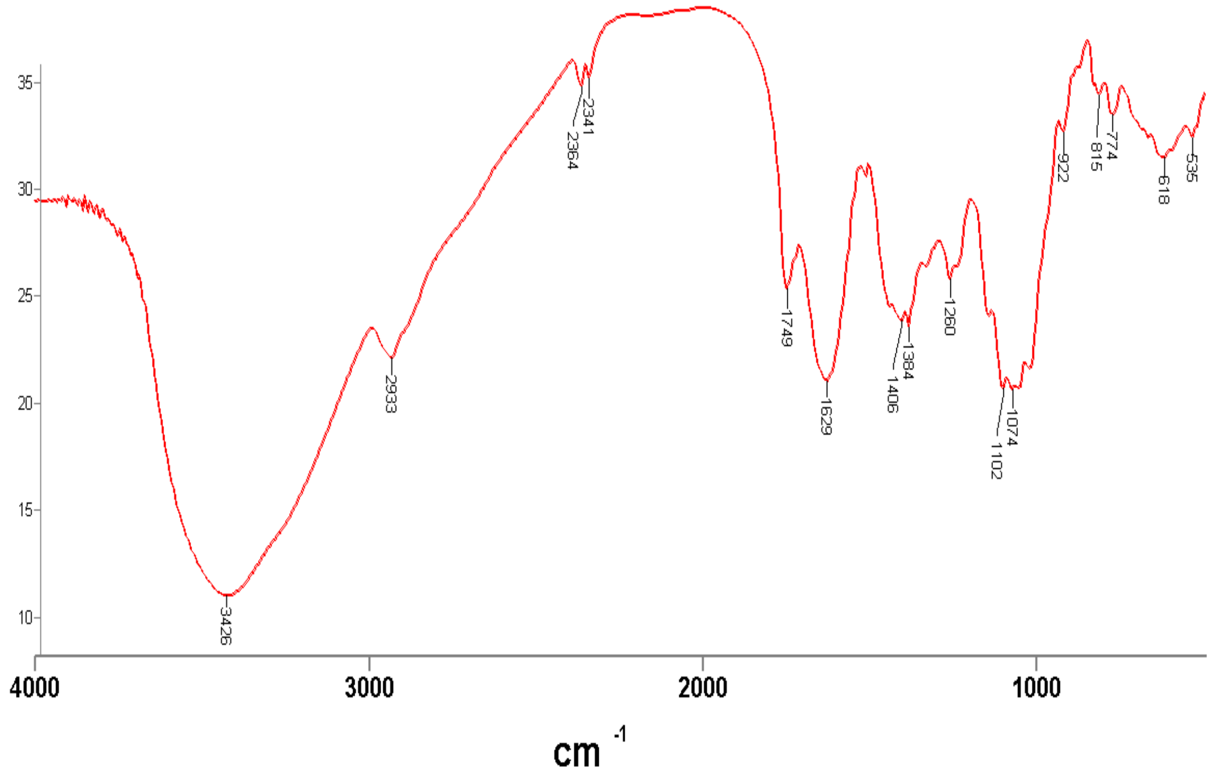


Figure 1. FT-IR spectrum of eggplant peel extract

The FT-IR shows strong absorption at 3426 cm^{-1} for OH stretching mode. The absorption at 2933 cm^{-1} is aromatic C-H band stretching mode. The peaks at 1749 and 1629 cm^{-1} correspond to the stretching modes of carbonyl group and C=C, respectively. The absorption at 1406 cm^{-1} can be assigned to the C=C stretching mode. The peaks at 1384 and 1250 cm^{-1} indicate the presence of C-SO_2-Cl and aryl OH. Finally, the absorptions at 1102 and 1074 cm^{-1} shows the stretching mode of C-O.

3.2 Weight Loss Measurements

The corrosion rate and inhibition efficiency of mild steel immersed in 2 M HCl solution at 25± 2°C after one week as a function of eggplant peel extract are shown in Figure 2. The corrosion rate decreases as the eggplant peel extract concentration increases up to 200 ppm. Above 200 ppm, the corrosion rate approximately remained constant. This can be attributed to the increase in adsorption of the eggplant peel extract molecules onto the mild steel surface. Above 200 ppm, the constant rate could be attributed to the competitive adsorption effect between inhibitor molecules and the metal surface (which is already covered with initial layers of molecules via the initial 200 ppm) and/or the withdrawal of the adsorbed extract to the bulk solution. The inhibition efficiency was calculated using equation 1above.

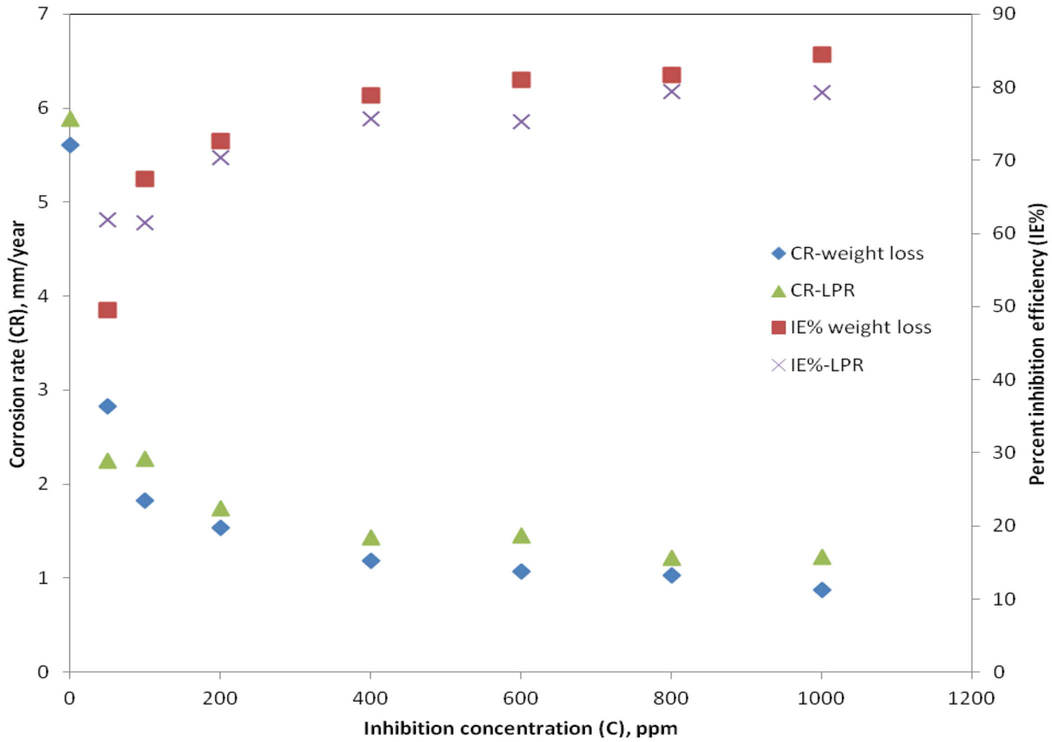


Figure 2. Corrosion rate and inhibition efficiency of mild steel specimens in 2M HCl with and without eggplant peel extract using the weight loss and LPR methods.

3.3 Mechanism of corrosion inhibition

The effectiveness of plant extracts as corrosion inhibitors can be attributed to the adsorption of the inhibitors molecules through the polar groups to the metal surfaces. The adsorbed layer on the metal surface acts as a barrier between the corrosive environment and the metal surface. Adsorption isotherms are employed to understand the inhibition mechanism of inhibitors on metal surfaces. They provide information about the adsorbed molecules interactions with the metal surface and the interaction between the adsorbed molecules. Surface coverage values were determined from the weight loss data assuming that the inhibition efficiency (IE%) to be directly proportional to the surface coverage *(θ)*. The surface coverage data were fitted to different adsorption isotherm models and the correlation coefficient (R^2) was used to decide on the best model. The best correlation for the eggplant peel extract data was obtained using Langmuir adsorption isotherm which is represented by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (2)$$

Where k is the adsorption constant, C is the inhibitor concentration and

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \qquad (3)$$

Where *R* is the universal gas constant, *T* is the absolute temperature and ΔG^0_{ads} is the standard free energy of adsorption.

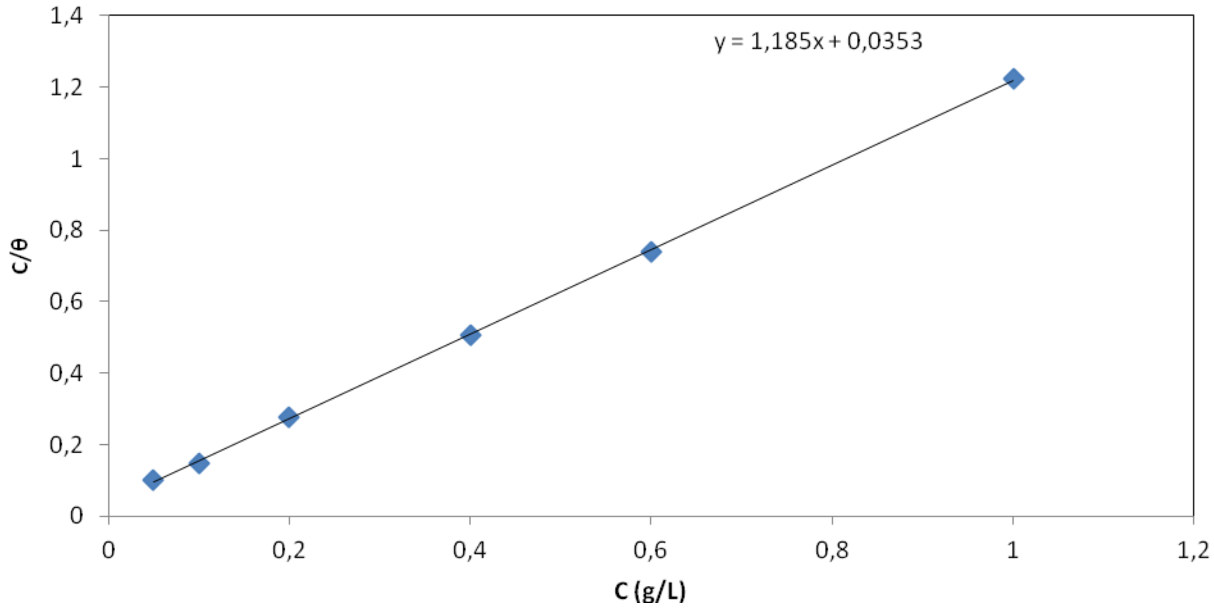


Figure 3. Langmuir isotherm for adsorption of eggplant peel extract onto mild steel surface in 2M HCl

Figure 3 shows the effect of the eggplant concentration in the solution (C) on the amount of inhibitor adsorbed on the metal surface (C/θ); values of C/θ vary linearly with C with almost unit slope indicating conformity to the Langmuir adsorption isotherm. The value of ΔG^0_{ads} as found from Fig. 3 is about -17.23 kJ/mole. The negative sign indicates that the adsorption is a spontaneous process and the value indicates a physical adsorption [25].

3.4 Electrochemical measurements

3.4.1 Linear polarization resistance (LPR)

LPR can be used to determine the corrosion rate using electrochemical means. For the LPR test, the start potential was 10 mV, and the finish -10 mV with respect to open circuit potential. It was shown that for small changes (±20 mV) from the free-corrosion potential, the relationship between the polarization resistance (R_p) and corrosion rate (CR) can be expressed by the following equation (26):

$$CR = \frac{\beta_a \beta_c M}{2.3(\beta_a + \beta_c) R_p F Z D} \quad (4)$$

Where β_a, β_c are the anodic and cathodic Tafel slopes, respectively, *M* is the molecular weight of the metal, *F* is Faraday's constant, *Z* is the metal's valence, and *D* is the metal's density. The inhibition efficiency was evaluated using the relationship:

$$IE\% = \frac{I_0 - I}{I_0} x100 \quad (5)$$

where I and I_0 are the current density of steel with and without inhibitor, respectively.

The corrosion rate of mild steel in 2M HCl is decreasing and the inhibition efficiency is increasing as the inhibitor concentration is increasing at room temperature (Figure 2). The overall behavior is similar to that observed by the weight loss method. Above 400 ppm, the corrosion rate and inhibition efficiency remained approximately constant.

Table 1. Kinetic parameters derived from LPR plots for mild steel metal specimen immersed in 2 M HCl with and without eggplant peels extract inhibitor.

T (°C)	C (ppm)	LPR (ohm*cm^2)	Icor (μA/cm^2)	CR (mm/year)	E (mV)	I.E%
25	0	40.94	510.00	5.89	-473.07	-
	50	105.3	190.00	2.24	-410.82	61.88
	100	101.5	195.74	2.27	-454.99	61.47
	200	127.7	150.60	1.75	-464.30	70.35
	400	164.4	123.62	1.43	-412.09	75.66
	600	154.9	125.29	1.45	-454.11	75.34
	800	183.8	104.76	1.21	-414.66	79.38
	1000	181.9	105.35	1.22	-417.66	79.26
40	0	12.36	2343.40	27.16	-478.32	-
	200	28.80	830.40	9.62	-471.10	64.56
	400	49.70	459.37	5.32	-474.47	80.40
	600	41.48	535.50	6.21	-471.63	77.15
50	0	6.52	5708.0	66.16	-461.03	-
	200	14.19	2021.3	23.43	-460.55	64.59
	400	18.89	1343.7	15.57	-460.73	76.46
	600	23.10	1190.1	13.79	-463.34	79.15

Table 1 shows that the LPR values are increasing in the present of inhibitor and the potential is shifted 9-63 mV anodically compared to the blank. An inhibitor can be described as being cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to the corrosion rate of the blank (27). LPR method was also employed to determine the effect of temperature on the corrosion inhibition properties of mild steel in 2M HCl at selective inhibitor concentration in the temperature range of 25-50±1°C.

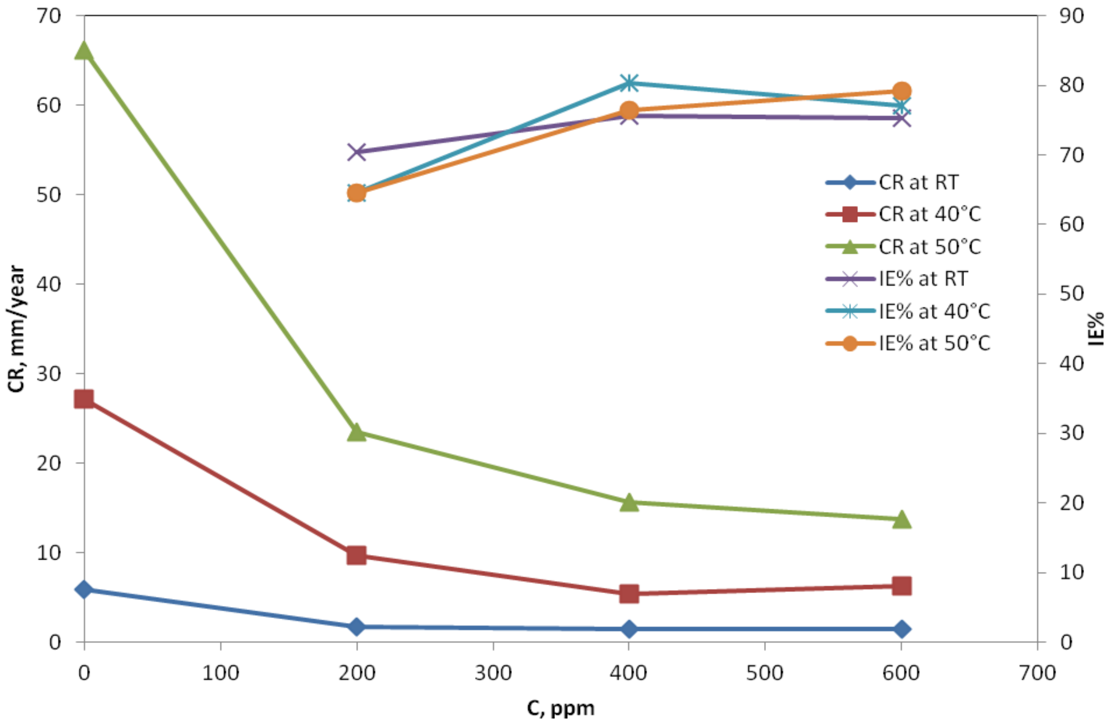


Figure 4. Corrosion rate and inhibition efficiency of mild steel in 2M HCl with and without eggplant peel extract at different temperatures using LPR.

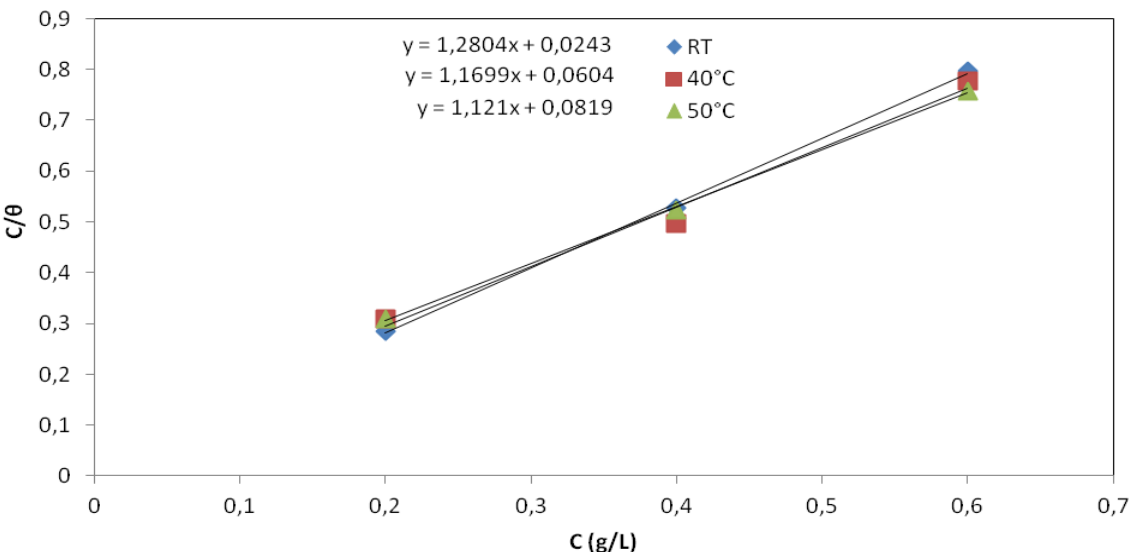


Figure 5. Langmuir isotherm for adsorption of eggplant peel extract onto mild steel surface in 2M HCl at different temperatures

Figure 4 shows that the corrosion rate increases as the temperature increases at all inhibitor concentrations. The corrosion rate remains constant for C≥400 ppm for all temperatures. A maximum of about 80% inhibition efficiency was observed at C ≥ 400ppm. Similar behavior was observed with the inhibition efficiency. In all cases, the inhibition efficiency slightly decreases with increasing in temperature and the activation energy slightly decreases with increasing inhibitor concentration. This behavior is an indication of the formation of an adsorption film of physical electrostatic nature [28]

The *C/θ* versus *C* were plotted for the various temperature levels based on the LPR results. Figure 5 shows that plots of *C/θ* versus *C* give straight line with almost unit slope at all temperatures. This again supports the previous observed behavior based on the weight loss method, i.e., the adsorbed eggplant peel extract on the mild steel follows Langmuir adsorption isotherm over the range of concentrations and temperature studied. The calculated values of ΔG^0_{ads} for the different temperatures are: -19.16 kJ/mole at 25°C; -17.76 kJ/mole at 40°C and -17.51 kJ/mole at 50°C. The negative signs indicate that the adsorption of eggplant peel extract onto the mild steel surface is a spontaneous process.

The activation energy of the corrosion reaction in presence and absence eggplant peel extract was calculated using Arrhenius equation:

$$CR = CR_0 exp\left(-\frac{E_a}{RT}\right) \qquad (6)$$

Where E_a is the apparent activation corrosion energy, *T* is the absolute temperature, CR_0 is the Arrhenius pre-exponential constant and *R* is the universal gas constant. Values of E_a were determined from the slope of the *ln(CR)* versus *1/T* plots at different inhibitor concentration (Figure 6).

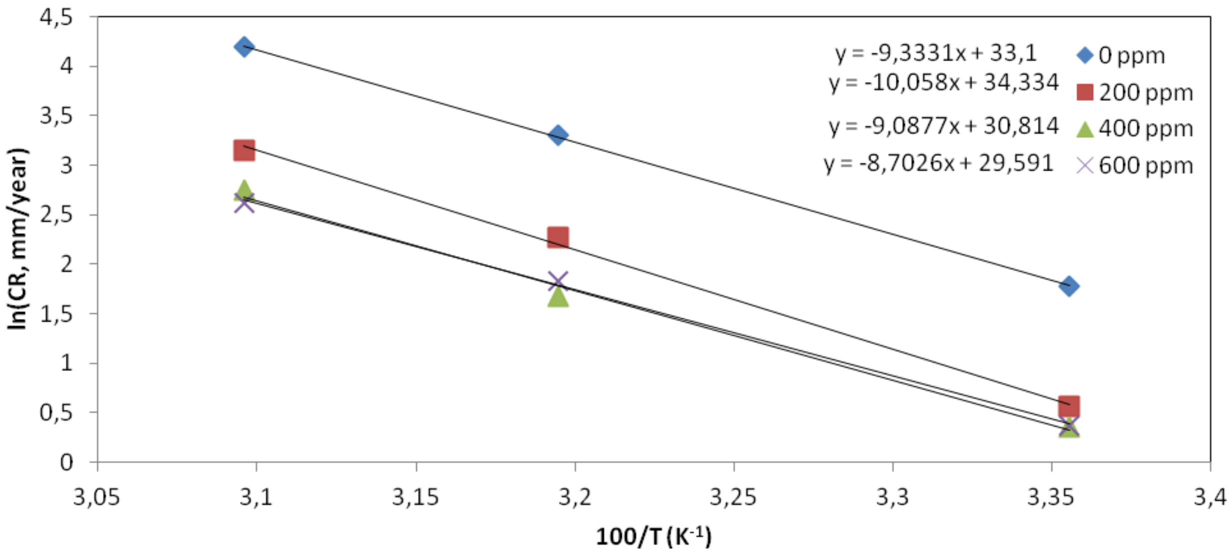


Figure 6. Arrhenius plots for the corrosion rate of mild steel in 2M HCl with and without eggplant peel extract at different temperatures.

As the concentration of eggplant extract increases from 0 to 600 ppm, E_a values initially increase, pass through a maximum, and then slightly decay down. Actually, E_a values found were: 77.57, 83.62, 75.56 and 72.35 kJ/mole corresponding to 0, 200, 400, and 600 ppm, respectively. Similar behavior was observed with the inhibition efficiency. This behavior is an indication the formation of an adsorption film of physical electrostatic nature [28]

3.4.3 Electrochemical Impedance Spectroscopy (EIS)

EIS was employed to further understand the kinetics and mechanism of the mild steel corrosion inhibition by the eggplant peel extract at 25°C.

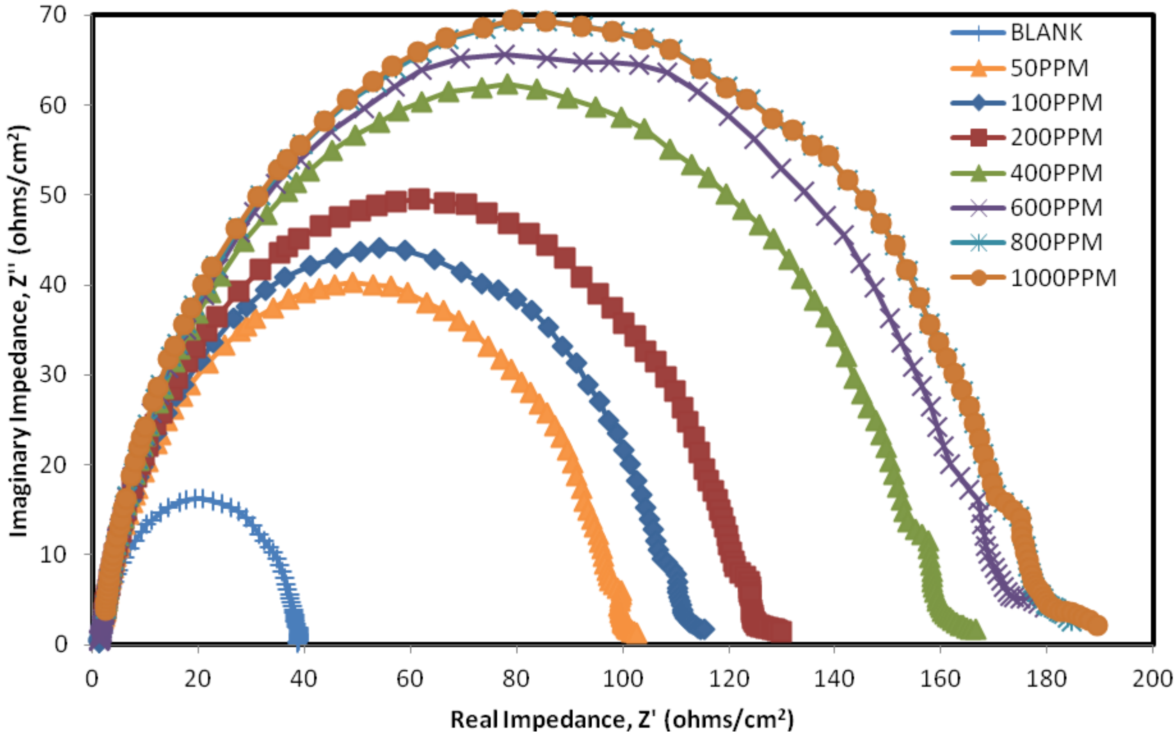
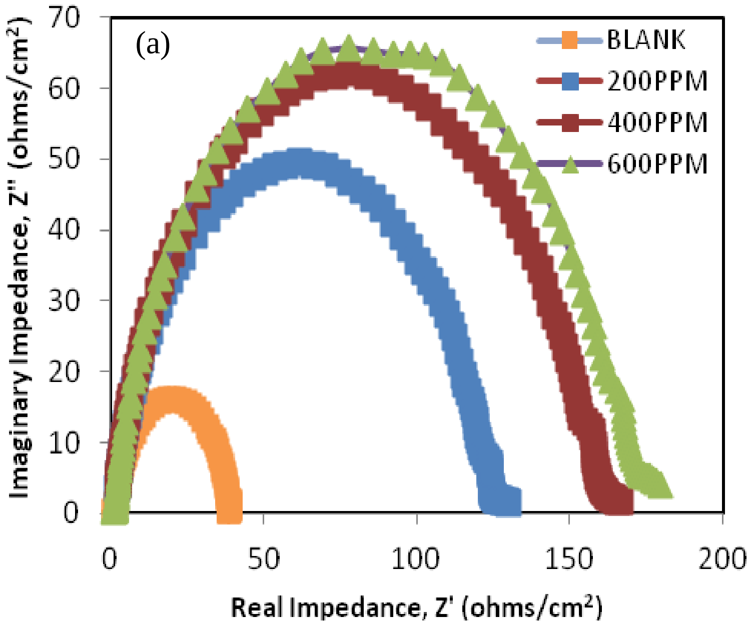


Figure 7. Impedance plots of mild steel in 2M HCl with or without eggplant peel extract.

Figure 7 shows the impedance response of mild steel in 2M HCl with the presence and absence of the inhibitor represented via Nyquist plots. The diameter of Nyquist plots increased on increasing the concentration of eggplant peel extract indicating strengthening of inhibitive film. The kinetic parameters derived from the Nyquist plots and the percentage inhibition efficiency are given in Table 2. As the concentration of inhibitor increased, the capacitance (C_{dI}) decreased and polarizing resistance (R_{ct}) increased. These results are in very good agreement with both weight loss and LPR data and can be attributed to a decrease in local dielectric constant and an increase in the thickness of the electrical double layer. This again suggests that the inhibitor molecules function by physical adsorption at the mild steel-solution interface [28].

Table 2. Kinetic parameters derived from EIS plots of mild steel immersed in 2 M HCl with and without eggplant extract at different temperature.

Temperature (°C)	C (ppm)	R_{ct} (Ωcm^2)	C_{dl} ($\mu F/cm^2$)	Icorr. mA/ cm^2	IE%
25	0	37.48	252.1	0.55	-
	50	98.06	145.1	0.21	62.5
	100	109.1	156.0	0.18	67.2
	200`	122.4	113.6	0.16	71.7
	400	157.0	113.8	0.13	76.7
	600	167.9	145.9	0.12	79.2
	800	174.6	111.3	0.11	80.1
	1000	174.7	110.4	0.11	80.2
40	0	10.93	894.0	2.65	-
	200	28.07	273.7	0.85	67.8
	400	49.15	205.9	0.47	82.4
	600	40.86	203.0	0.54	79.5
50	0	5.01	719.5	7.44	-
	200	13.54	518.1	2.12	71.5
	400	18.51	165.5	1.37	81.6
	600	20.21	275.1	1.36	81.7



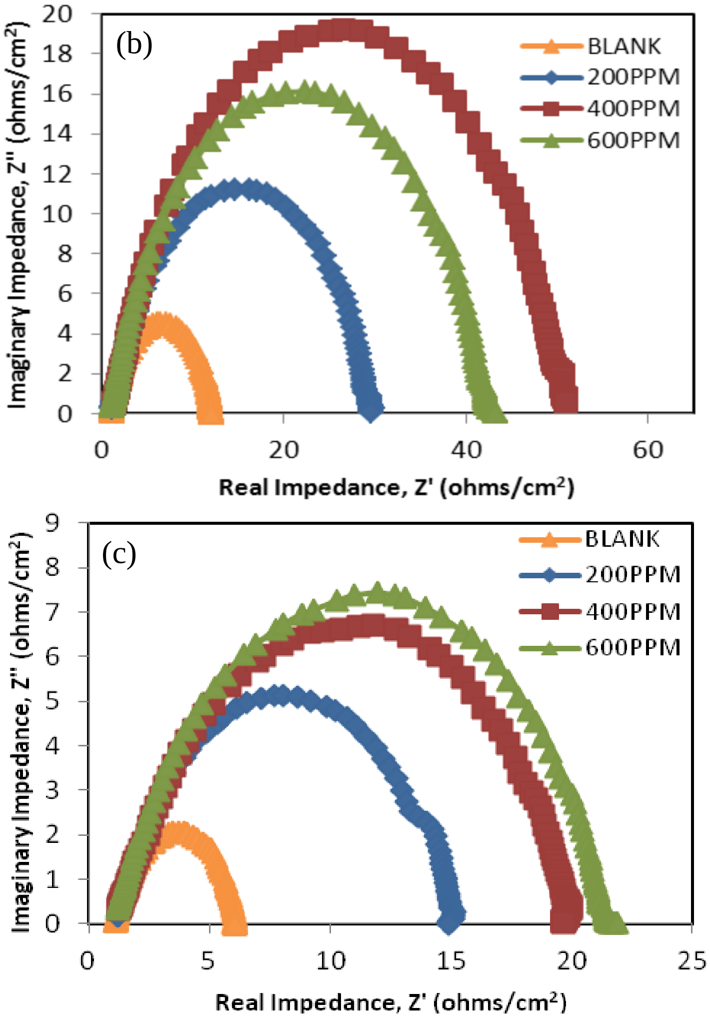


Figure 8. Impedance plots of mild steel in 2M HCl with or without eggplant peel extract at (a) 25°C, (b) 40°C and (c) 50°C.

EIS measurements were also performed for mild steel in 2M HCl with the presence and absence eggplant peel extract at 40-50°C (Figure 8). As can be seen from the Nyquist plots, the diameter increases as the concentration of inhibitor increased. Table 2 shows that the R_{ct} values increased and C_{dl} values decreased indicating decrease in the formation of anodic process controlling intermediates from the mild steel dissolution and subsequently inhibition corrosion and the decrease in the capacitance values may be attributed to the formation of a protective layer at the mild steel surface [29]. Similarly as before, the inhibition efficiency is increased as the inhibitor concentration increased at all temperatures.

3.4-4 Potentiodynamic polarization, Cyclic Sweep (CS)

The inhibition of eggplant peel extract on mild steel specimens immersed in 2M HCl was further studied by measuring the change in the cathodic and anodic behaviors of the specimens which correspond to hydrogen reduction and metal oxidation. The cyclic sweep was recorded at scanning sweep rate of 60mV/min.

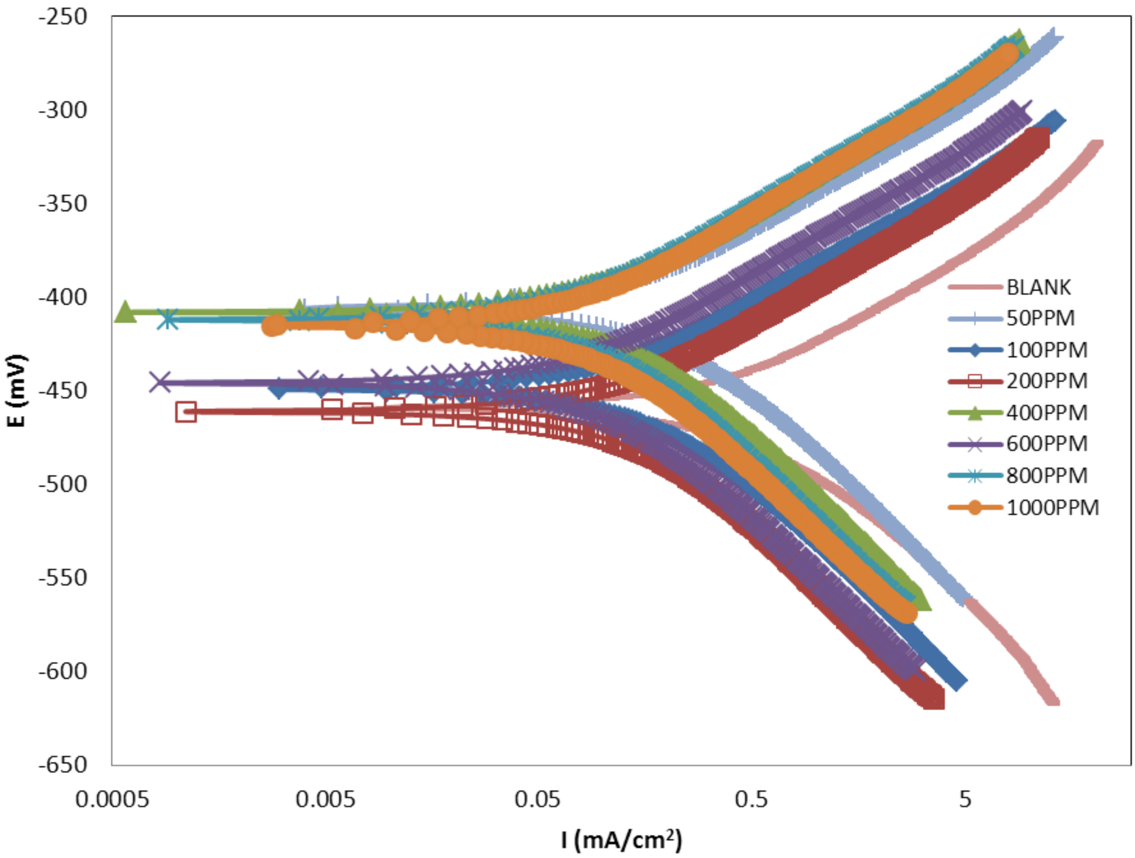


Figure 9. Cyclic sweep of mild steel immersed in 2M HCl with or without eggplant peel extract at room temperature.

The plot of the cell potential (mV) versus current density (mA/cm^2) in Figure 9 and Table 3 show that the current density decreased with increasing extract concentrations. This phenomenon corresponds to a decrease in the corrosion rate which can be explained by the shift of the cathodic and anodic Tafel slopes. It is also noticed in Figure 9 that there a clear shift for both anodic and cathodic parts for the sweeps at the various test concentrations. The shift range in the anodic Tafel slopes of the tests is more noticeable than the shift range in the cathodic Tafel slopes; this indicates that the decrease of the oxidation rate of the metal with higher extract concentrations corresponds to the relative drop in the corrosion rate. The extract adsorption on the metal surface is causing the decrease in the metal dissolution at a relatively more noticeable/higher rate while affecting the hydrogen reduction to a lesser extent.

As before 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 [27]. This and the shifts in both anodic and cathodic curves indicate that the eggplant peel extract is a mixed inhibitor with significant anodic efficiency.

Table 3. Kinetic parameters derived from Tafel slope plots for mild steel metal specimen immersed in 2 M HCl with and without eggplant peels extract inhibitor.

T (°C)	$C_{inhibitor}$ (ppm)	E_{corr} (mV vs. SCE)	I_{corr} ($\mu A/cm^2$)	β_c (mv/Dec)	β_a (mv/Dec	IE%
25	0	-449.0	227.6	109.55	84.89	-
	50	-410.3	107.4	115.90	78.80	52.8
	100	-455.2	76.8	112.49	76.96	66.3
	200	-464.3	92.9	109.19	74.33	59.2
	400	-411.8	72.4	113.85	79.30	68.2
	600	-449.8	58.9	109.46	75.39	74.1
	800	-415.3	62.6	109.82	74.21	72.5
	1000	-418.9	57.5	107.70	74.58	74.7
40	0	-475.8	708.5	146.21	122.31	-
	200	-467.6	486.8	129.05	95.88	31.3
	400	-473.3	285.6	121.74	93.34	59.7
	600	-470.1	309.9	122.25	87.77	56.3
50	0	-458.5	1536.8	184.55	159.66	-
	200	-458.8	825.3	154.69	115.01	46.3
	400	-457.9	776.5	138.29	101.07	49.5
	600	-466.0	578.6	154.83	106.85	62.4

Currently, there are few investigators who reported the use of fruit and vegetable peels' as corrosion inhibitors [22, 30-31]. The eggplant peel extract in 2M HCL proved to have good inhibition efficiency when compared to plant leaves extract reported in literature (6-15). In addition, it shows higher corrosion inhibition efficiency than those of banana, mango, orange, passion fruit and cashew peels extracts [22, 30-31].

4. CONCLUSIONS

- The inhibition efficiency of mild steel in 2M HCL increases with increasing concentration of eggplant peel inhibitor. Inhibition efficiency of 84% was achieved.
- The inhibition efficiency at higher temperatures increases with an increase in the inhibitor concentration.
- AC impedance results showed that charge transfer resistance increases and the capacitance decreases with increase in the eggplant peel extract concentration.

- The eggplant peel extract act as a mixed type inhibitor on the metal surface.
- The active inhibitor was found to follow the Langmuir's adsorption isotherm.

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