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Corrosion Inhibition of Mild Steel using Fig Leaves Extract in Hydrochloric Acid Solution

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The inhibition effect of Fig leaves extract on corrosion of mild steel in 2M acid solution was investigated using traditional weight loss measurements and various electrochemical techniques. Corrosion inhibition efficiency of Fig leaves extracts was evaluated using weight loss measurements for effect of various solution concentrations. In addition, electrochemical techniques were performed to evaluate both concentration and temperature changes of test solution. Nyquist plots showed that the higher the Fig leaves extract concentration, the higher the charge transfer resistance and the lower the value of the double layer capacitance. Both weight loss and electrochemical results showed similar trend indicating that Fig leaves extracts adsorption on mild steel followed the Langmuir adsorption isotherm at all test temperatures. The change in free energy and the activation energy values indicate that the adsorption is physical. Inhibition efficiency of as high as 87% were achieved for Fig leaves extract of above 200 ppm.

Keywords: Adsorption, Langmuir isotherm; Corrosion inhibition; Corrosion; Natural inhibitors; Fig; Mild-steel

1. INTRODUCTION

Several protective measures are taken to control/prevent corrosion, one of them being the use of inhibitors [1-6]. A corrosion inhibitor is a substance which, when added to a corrosive environment, significantly decreases the rate of corrosion attack caused by the environment. Corrosion inhibitors are commonly added in small amounts to pickling acids, acid stimulation fluids, cooling waters, oil and gas production streams, either continuously or intermittently to control corrosion. Corrosion inhibitors generally control corrosion by forming various types of films that modify the environment's corrosivity at the metal surface. Inhibitors form films in several ways: by adsorption, the formation of bulky precipitates, and/or the formation of a passive layer on the metal surface. Some inhibitors retard corrosion by adsorption to form a thin, invisible film only a few molecules thick. Others form bulky precipitates that coat the metal and protect it from attack. A third mechanism consists of causing the metal to corrode in such a way that a combination of adsorption and corrosion product forms a passive layer.

Several heterocyclic organic compounds [7-10] have been reported as corrosion inhibitors. The corrosion inhibition property of organic compounds having hetero atoms such as N, S and O of high electron density is already established. But, most of the synthetic organic inhibitors are toxic in nature which pause various threats when discharging at the various streams. This is a recent concern for most of chemical suppliers and operators who have to comply with the increasingly more stringent rules and regulations that minimize impact of the chemicals to nature, humans, aquatic life and other creatures sharing with us this universe. This has led to exploring and the increase demand on using natural originating products which would have better chances of being eco-friendly and harmless. Recently, many eco-friendly corrosion inhibitors have been developed [11-22]. For example, Datura metel [18], Datura stramonium [19], Atropine sulphate [20], Black pepper [21] and Strychno nux-vomica [22] were successfully reported for their anticorrosion properties. The observed results showed that all the above said plants have excellent anticorrosion effect and most importantly eco-friendly.

Fig leaves extract was recently tested as antiscalent for $CaCO_3$ calcareous deposits [23]. Abdel-Gaber et. al. showed that Fig leaves extract is effective as antiscalent. In this work, Fig leaves extract was investigated for its effectiveness as a natural inhibitor to prevent corrosion of mild steel in 2M HCl using the weight loss and electrochemical techniques measurements.

2. EXPERIMENTAL

2.1.1. Preparation of Plant Extract

Fresh leaves of Fig plant were washed under running water, dried using a fluidized bed dryer for 1 h, grinded to powder. Extraction of the Fig inhibitor was done using double distilled water and refluxing the solution for two hours. After cooling, a vacuum filtration of the water-Fig mixture was applied to retain the Fig inhibitor extract. The concentration of the inhibitor extract solution (Stock solution) concentration was determined to be approximately 1.4 weight % (14324 ppm). Desired more dilute test concentrations were prepared from the stock solution.

2.1.2 Preparation of Mild Steel Specimens

Mild steel C1018 coupons used for this study were with the chemical composition of 0.036% Al, 0.18% C, 0.02% Cr, 0.02% Cu, 0.85% Mn, 0.01% Ni, 0.01% P, 0.02% Si and the balance Fe. The specimens of 50 x 25 x 1.5 mm were used for weight loss measurements. Circular surface of 1 cm^2 coupons were used for the electrochemical measurements. The sample electrodes were mounted in

Teflon cell. The exposed surface area of the metal was 1 cm^2. The specimens were degreased using methanol, washed thoroughly with doubled distilled water, dried in oven and immediately used.

2.1.3. Test Solution- Electrolyte

A solution of 2M concentrated acid was prepared using double-distilled water and AR grade hydrochloric acid. The concentration of the extracted inhibitors in the aerated hydrochloric acid test solution varied from 50 to 1000 ppm.

2.2.1 Weight Loss Method

Pre weighed mild steel coupons were left hanging using Teflon in glass beakers containing 2M HCl with 0 to 800 ppm inhibitor for 1 week at room temperature (25 ± 2°C) before loss of weight was recorded. The corrosion rate was calculated in millimeter per year, (mm/yr) on the basis of the apparent surface area. The inhibition efficiency measurements were based on the weight loss at the end of the measuring period. The percentage inhibition efficiency (IE%) was calculated using the equation:

$$\mathrm{IE\%} = \frac{(W-W_I)}{W} \mathrm{X}\ 100 \qquad (1)$$

Where W and W_I are the corrosion rates of steel coupons in the absence and presence of plant extracts, respectively.

2.2.2 Electrochemical Measurements

A three electrodes cell system containing working electrode (mild steel coupon) of a 1 cm^2 exposed area, saturated calomel electrode as a reference and the a platinum electrode as auxiliary were used. All electrochemical experiments were performed at room temperature (25 ± 2°C) in 2M HCl electrolyte solution with and without extracted inhibitor using Gill AC potentiostat manufactured by ACM Instruments. Three different electrochemical tests were conducted, linear polarization resistance (LPR), Potentiodynamic scans (cyclic sweep polarizations, CS) and electrochemical AC impedance spectroscopy (EIS). A linear polarization test was carried out by a scan from approximately -10mV to +10mV with respect to working electrode rest potential. The cyclic sweep polarization also took in consideration open circuit potentials of working electrode and started at a relatively cathodic potential and scanned towards the anodic direction, E = ± 300 mV with a scan rate of 1mV/s. EIS measurements were performed using AC signal amplitude of 20 mV peak to peak in the frequency range of 0.1 Hz to 1kHz. The inhibition efficiency (IE) was determined using the equation

$$\mathrm{IE} = \left[\frac{(I-I_i)}{I}\right] \mathrm{x}100 \qquad (2)$$

Where I and I_i are the corrosion current densities without and with inhibitor, respectively.

3. RESULTS AND DISCUSSION

Some natural inhibitors not only can inhibit corrosion, but also they can be used as Antiscalents. The Fig leaves extract which was used in this experiment as a corrosion inhibitor can serve as a scale inhibitor as well. The Fig extract has the ability to impede the process of supersaturation which leads to scaling because the extracted molecules of the Fig leaves have the ability to get adsorbed onto the active sites growing crystals (due to precipitation) which results in dispersing the suspended solids and to get them liquefied reducing the rate of the growth in crystallization. Some of the effective chemical molecules in the Fig extract to which the latter behavior is attributed to are Psoralene, Bergabten, Vanillic and β-Sitosterol. Due to their containment of multiple lone pair of electrons, multiple bonds and/or conjugated Π-type bond system, these molecules contribute towards inhibition [23]. Adsorption of these active molecules forms thin inhibitor films on the metal surface which in order relatively isolate the metal surface from the corrosive environment causing much reduced corrosion rates. Inhibition efficiency of these films depends on various factors including but not limited to corrosivity of the environment, concentration of the active inhibitor molecules, any synergetic effects with other molecules present in the environment and/or flow/shear effects.

3.1. Weight Loss Measurements

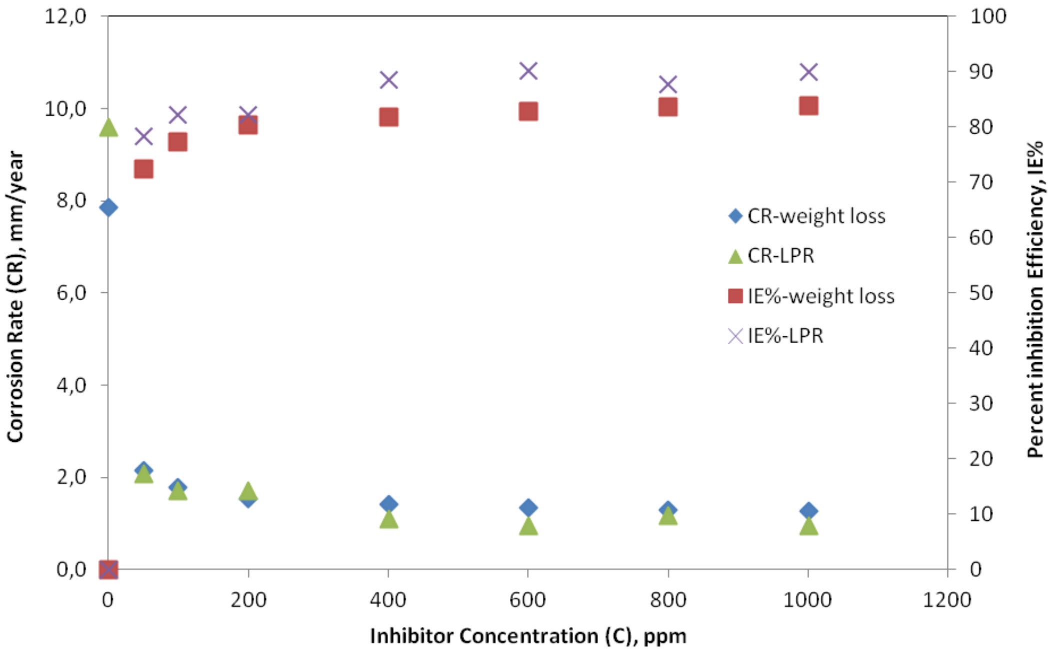

Figure1. Corrosion rate and inhibition efficiency of mild steel specimens in 2M HCl with and without Fig extract using on the weight loss and LPR methods.

Fig. 1 shows the corrosion rate (mm/yr) and the inhibition efficiency for mild steel specimens immersed to 2M HCl for 7 days as a function of inhibitor concentration at room temperature. The results show that the corrosion rate decreased as the concentration of Fig leaves extract increased (up to approximately 400 ppm). This behavior is attributed to higher adsorption level of active inhibitor molecules from the extract on the metal surface. For Fig extract concentrations higher than 400 ppm, the corrosion rate remained approximately constant. This could be an indication that the 400 ppm concentration is approximately the optimum inhibitor concentration. Higher extract concentrations did not show any additional significant protection under these particular lab test conditions and hence has it is to be evaluated for its cost performance when applied under real industrial applications. The inhibition efficiency was calculated based on the weight loss method (Equation 1). The inhibition efficiency showed a linear relation with increase in the extract concentration. Inhibition efficiency as high as 85 % was achieved for test solutions contained 400 ppm of Fig extract.

3.2 Adsorption Mechanism

The observed increase in inhibitor efficiency as the inhibitor concentration increases could be attributed to various inhibition mechanisms. For instance, the inhibitor could form a thin layer on the metal coupon and partly protect it. Adsorption isotherms are used to understand the mechanism of corrosion inhibition of metals and alloys. Assuming that the adsorption of Fig leaves extract molecules was mainly due to a monolayer adsorption and ignoring the interaction between the adsorbed molecules, then the Langmuir adsorption isotherm can be employed. A central parameter in Langmuir adsorption is the fraction of the coupon surface that is covered by an inhibitor, θ=IE%/100. If this adsorption method is applicable, then the inhibition efficiency, IE%, should be in direct proportion with θ: the higher the surface coverage with inhibitor molecules, the fewer sites would be available for corrosion. In order to test whether the inhibitor extracted from Fig follows the Langmuir adsorption isotherm, the collected data was fitted according to the Langmuir equation. The Langmuir equation has some inherent assumptions employed in its development. as it is assumes that a fixed number of adsorption sites exist on the metal surface. Also, the equilibrium constant involved is assumed to be independent of θ if the enthalpy of adsorption is also independent of θ. The Langmuir adsorption mathematical relation can be expressed in many forms, but the one utilized in this analysis is as follows:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{3}$$

Where K is adsorption equilibrium constant.

Fig. 2 shows that a plot of C/θ vs. C gives a straight line with almost unit (1.1) slope. This implies that the adsorbed inhibitor on the mild steel surface follows Langmuir adsorption isotherm. The standard free energy (ΔG^0_{ads}) can be determined from the intercept of equation 3 and using equation 4.

$$k = \frac{1}{55.5}\exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \tag{4}$$

Where R is the gas constant and T is the absolute temperature. The ΔG^0_{ads} value was found to be -20.8 kJ/mole.

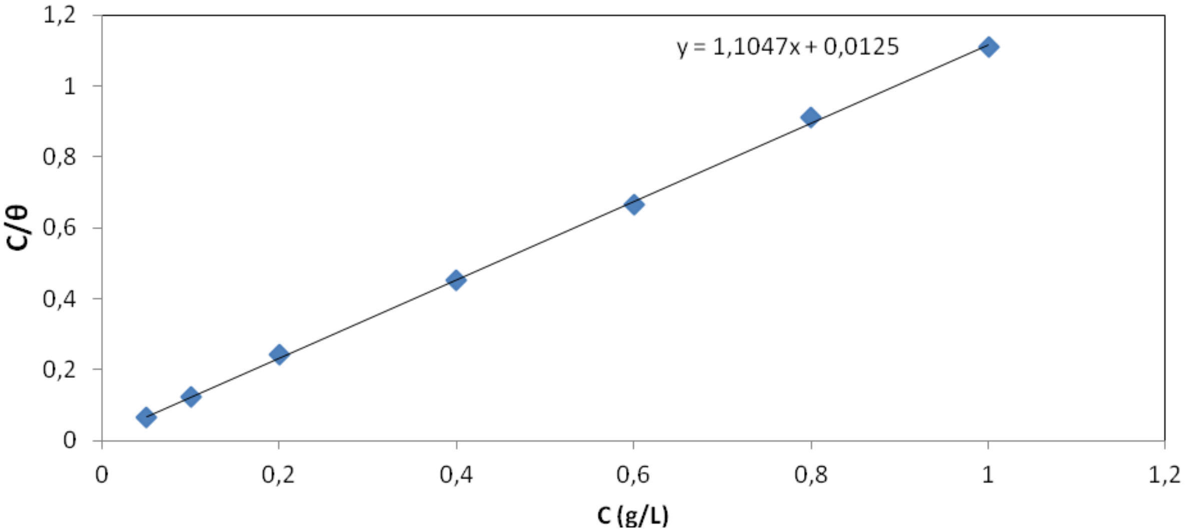

Figure 2. Langmuir isotherm for adsorption of Fig extract onto mild steel surface in 2M HCl.

The negative sign implies that the adsorption of the inhibitor onto the mild steel surface is a spontaneous process. The ΔG^0_{ads} value indicates that the adsorption is physical. If the values of ΔG^0_{ads} is in the order of -20 kJ/mole or less this would indicate a physical adsorption, while those values of -40kJ/mole or higher imply chemical adsorption which involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a physical bond [24].

3.3.1 Linear Polarization Resistance (LPR) Measurements

LPR was used to determine the corrosion rate as function inhibitor concentration and temperature. The corrosion rate (CR) can be calculated using the following equations:

$$CR = \frac{I_{cor}M}{F\,Z\,D} \tag{5}$$

$$I_{cor} = \frac{\beta_a\beta_c}{2.3\,R_p(\beta_a+\beta_c)} \tag{6}$$

Where β_a, β_c are the anodic and cathodic Tafel slopes, respectively, I_{cor} is the corrosion current density, M is the molecular weight of the metal, F is Faraday's constant, Z is the metal's valence, D is the metal's density and R_p is the polarization resistance.

LPR results (Fig. 1) show that the CR of mild steel in 2M HCl decreased as the Fig leaves extract concentration increased. The CR dropped sharply when inhibitor was introduced. The drop in corrosion rate was significant when small concentrations as small as 50, 100, 200 and 400 ppms were introduced. This criterion of fast action is very important for industry as speed of inhibition is usually expected. For concentration of 400 ppm and higher, the corrosion rate did not show any significant decrease and remained approximately constant. The inhibition efficiency increased as the inhibitor concentration increased. An inhibition efficiency as high as 90 % was achieved for 600 ppm. LPR results duplicated the same trend obtained from weight loss method.

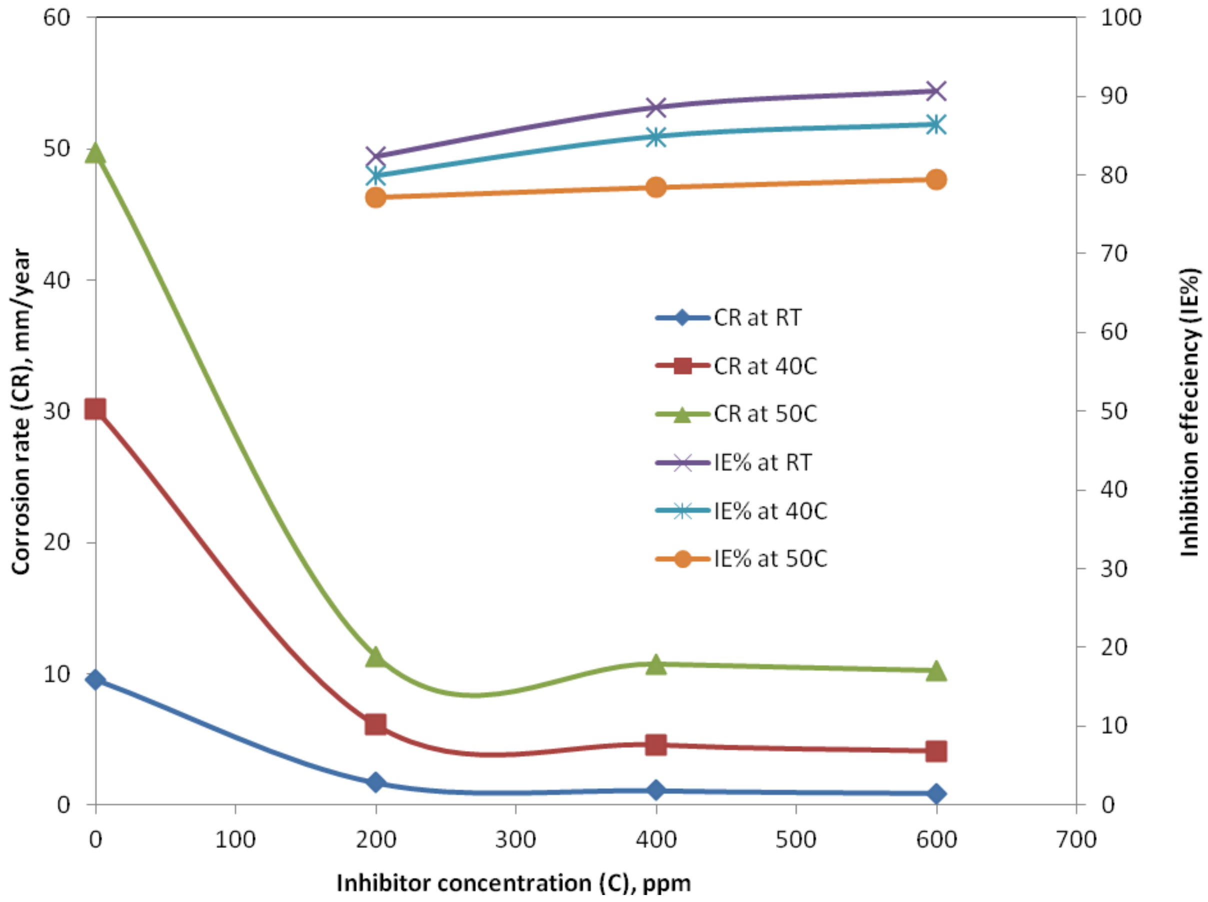

Figure 3. Corrosion rate and inhibition efficiency of mild steel specimens in 2M HCl with and without Fig extract at different temperatures using LPR

LPR measurements were also used to study the effect of temperature on the corrosion inhibition of mild steel in 2M HCl at selective inhibitor concentrations in the temperature range of 25-50°C. The calculated corrosion rate and inhibition efficiency are shown in Fig. 3. As expected, when the temperature increases the corrosion rate increased and the inhibition efficiency decreased. The slope of the curve gradually increased as the temperature increased, which seems to indicate a physical absorption. Inhibition efficiencies ranged between 80-90% over the temperature and test concentrations ranges.

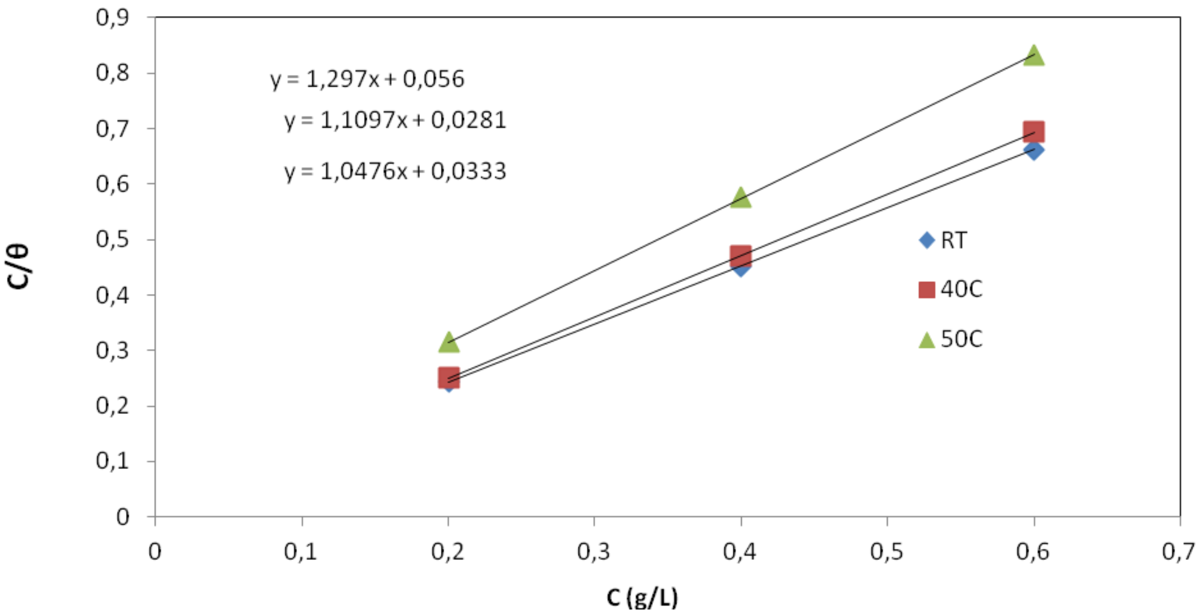

Figure 4. Langmuir isotherm for adsorption of Fig leaves extract onto mild steel surface in 2M HCl at different temperatures.

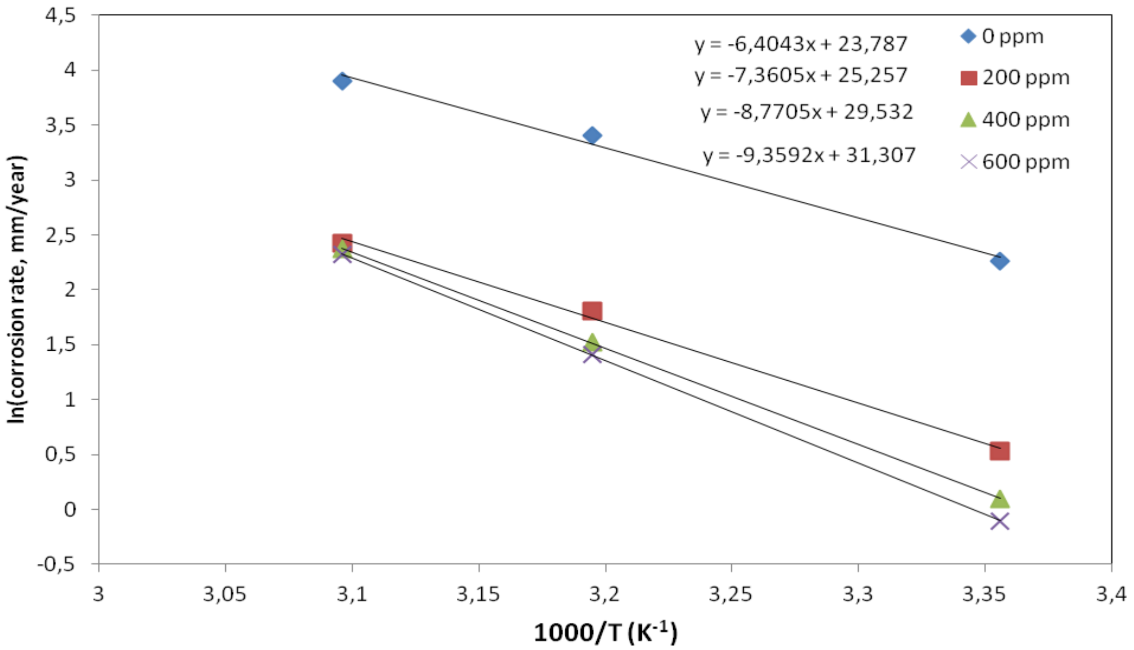

Figure 5. Arrhenius plots for the corrosion rate of mild steel in 2M HCl with and without Fig leaves extract at different temperatures

The C/θ versus C at the various temperatures were plotted (Fig. 4). All plots give straight lines with almost unit slope. This supports the observed behavior obtained using the weight loss method. This behavior confirmed that the adsorption Fig leaves extract obeys Langmuir adsorption isotherm. The calculated ΔG^0_{ads} values at the different temperatures based on the LPR method are:-17.09 kJ/mole at 25°C; -19.5 kJ/mole at 40°C and -19.92 kJ/mole at 50°C. The negative signs indicate that the adsorption of Fig leaves extract to the mild steel surface is spontaneous process. This is in full agreement with both weight loss and electrochemical results. Furthermore, the ΔG^{0}_{ads} values imply that the adsorption is again physical.

The activation energy of the corrosion reaction in the studied range of temperature was calculated using Arrhenius equation:

$$CR = K\exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

Where E_a is the apparent activation corrosion energy, T is the absolute temperature, K is the Arrhenius pre-exponential constant and R is the gas constant. The activation was determined by plotting the logarithm of the corrosion rate versus 1/T in the absence and the presence of Fig leaves extract (Fig. 5). The calculated values are: 53.24 kJ/mole at 0 ppm; 61.20 kJ/mol at 200 ppm; 72.96 kJ/mole at 400 ppm and 77.81 kJ/mole at 600 ppm. The increased in the activation energy as the concentration of Fig leaves extract inhibitor increased imply a physical molecular adsorption for the inhibitor on the mild steel surface.

3.3.2 Potentiodynamic Scans, Cyclic Sweep (CS)

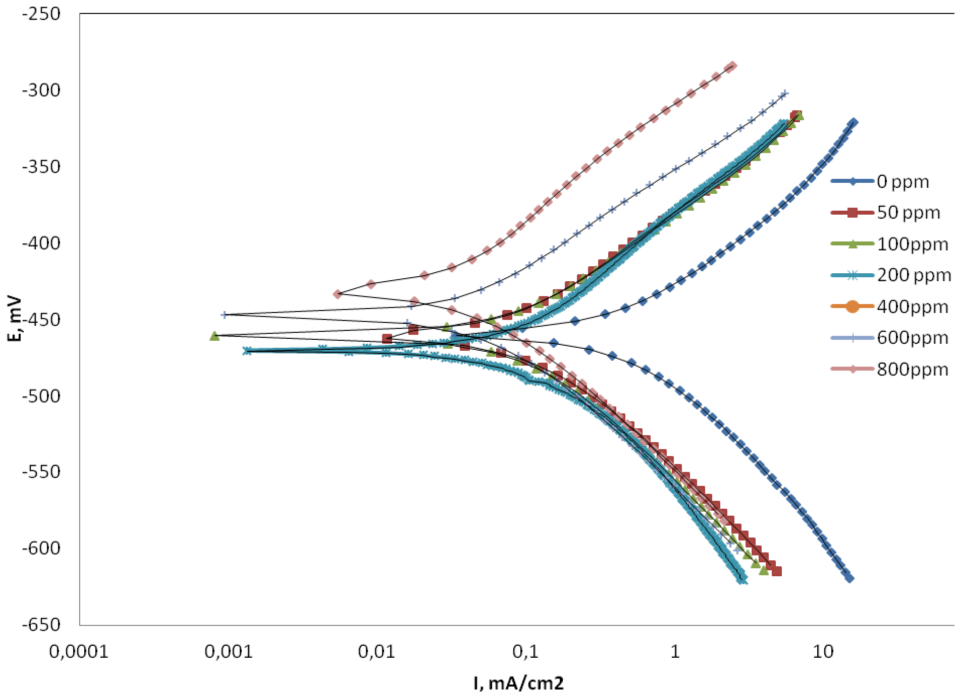

Figure 6. Cyclic sweep of mild steel immersed in 2M HCl with or without Fig leaves extract at room temperature

The inhibition of Fig leaves extract on mild steel samples in 2M HCl was also investigated by measuring the change in the cathodic and anodic behaviors of the specimens which correspond to hydrogen reduction and metal oxidation. The cyclic sweeps were conducted at a sweep rate of 1mV/sec.

Table 1. Kinetic parameters derived from Tafel slope plots for mild steel metal specimen immersed in 2M HCl with and without Fig extract inhibitor at 25°C.

C_{Fig} (ppm)	E_{corr} (mV vs. SCE)	I_{corr} (μA/cm^2)	β_c (mv/Dec)	β_a (mv/Dec	CR (mm/year)	IE%
0	-469	1242.9	96.8	91.5	14.41	0
50	-466	237.5	73.2	59.8	2.75	80.9
100	-464	240.1	72.0	66.4	2.78	80.7
200	-416	388.9	67.9	130.4	4.51	68.7
400	-467	157.7	66.5	76.5	1.83	87.3
600	-451	157.5	63.9	81.6	1.83	87.3
800	-479	162.5	78.7	76.8	1.88	87.0

Fig. 6 and Table 1 show that both the rate of cathodic and anodic reactions are reduced as the concentrations of inhibitor increased by reducing the current densities on both sides of the polarization curves. The reduction in current densities results in overall reduction in the corrosion rate. It is noticed in Fig. 6 that the shift range in the anodic Tafel slopes of the tests with different extract concentrations is higher than the shift range in the cathodic Tafel slopes; this indicates that the decrease in 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 while not affecting the hydrogen reduction. It can also be seen from Table 1 that the corrosion rate decreases and the inhibition efficiency increases as the inhibitor concentrations increases. The rate of corrosion and inhibition efficiency remained almost constant for inhibitor concentrations above 200 ppm.

3.3.3 Electrochemical Impedance Spectroscopy (EIS)

The inhibition process of Fig leaves extract was also investigated by the EIS. The EIS was performed over the frequency range from 10 kHz to 10 mHz at different test temperatures (25-50°C). Impedance measurements presented in the Nyquist format for mild steel immersed in 2M HCl with and without inhibitor are shown in Fig. 7, Fig. 8 and Table 2. The impedance diagrams are semicircles and the presence of inhibitor does not change their profiles. This behavior indicates that the charge transfer process mainly controls the corrosion of the mild steel. The diameter of Nyquist plots increased with increasing the concentration of Fig leaves extract indicating strengthening of inhibitive film. The impedance parameters derived from the Nyquist plots and percentage inhibition efficiency are given in Table 2. The inhibition efficiency was calculated based on the charge transfer resistance by:

$$IE\% = \frac{R_{ct} - R'_{ct}}{R_{ct}} x100 \qquad (8)$$

Where R_{ct} and R'_{ct} are the charge transfer resistance values with and without Fig leaves extract. As the concentration of inhibitor increased, the double layer capacitance (CdI) decreased and polarizing resistance (R_{ct}) increased.

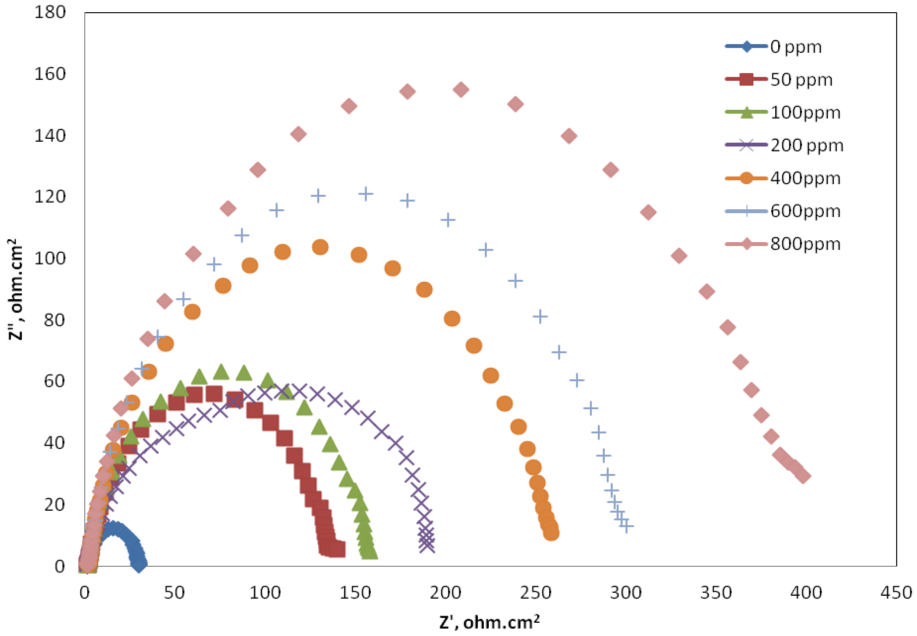

Figure 7. Impedance plots of mild steel in 2M HCl with or without Fig leaves extract.

Table 2. Kinetic parameters derived from EIS plots of mild steel immersed in 2M HCl with and without inhibitor at various test temperatures.

Temperature °C	C_{Fig} (ppm)	R_{ct} (Ωcm^2)	C_{dI} ($\mu F/cm^2$)	IE%
25	0	27.9	401.3	0
	200	199.7	381.6	86.0
	400	258.4	177.4	89.2
	600	198.3	178.5	86.0
40	0	8.7	685.3	0
	200	48.4	271.7	82.0
	400	69.9	186.7	87.6
	600	61.7	204.2	85.9
50	0	4.5	1161.0	0
	200	25.1	333.6	82.1
	400	26.7	241.0	83.1
	600	28.7	295.5	84.3

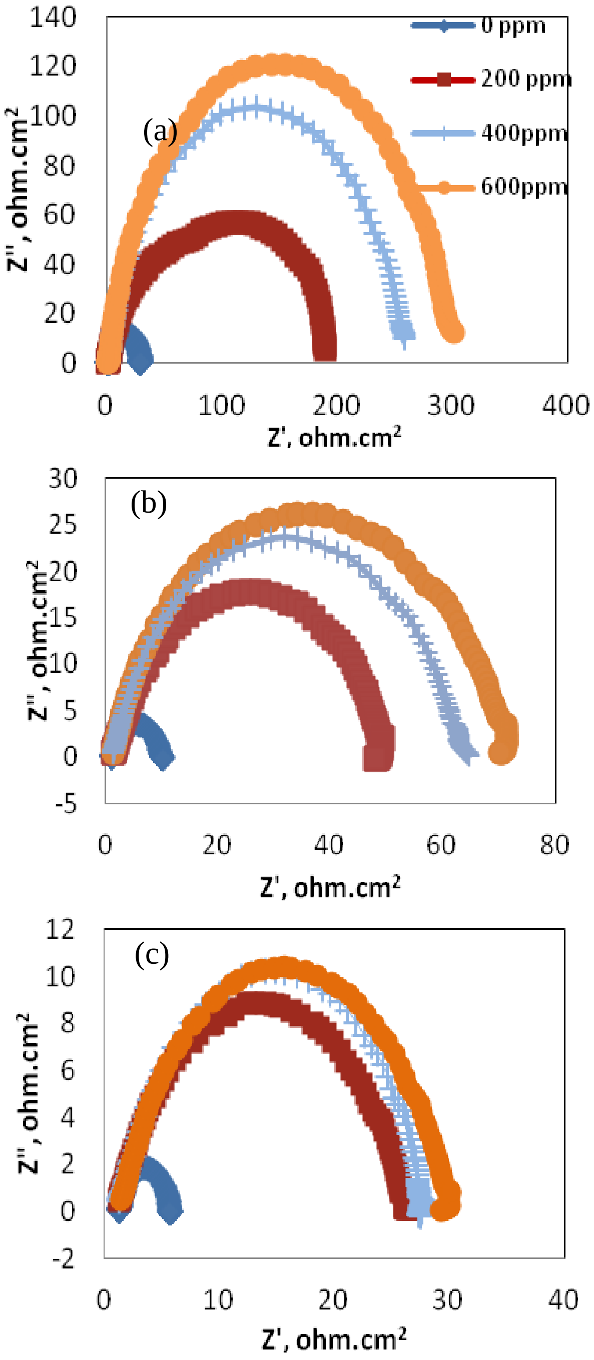

Figure 8. Impedance plots of mild steel in 2M HCl with or without Fig leaves extract at (a) 25°C, (b) 40°C and (c) 50°C.

These results can be related and to a reduction in local dielectric constant and increase in the thickness of the electrical double layer which again suggests that the inhibitor molecules function by adsorption at the mild steel-solution interface [25]. The overall inhibition efficiency increased as the Fig leaves extract concentration increased which is in a good agreement with all the observed results obtained by other techniques such as the weight loss, LPR and potentiodynamic sweeps. In terms of the stability, Fig leaves extract appears to be stable over time. Over a month period, the inhibition activity of the Fig leaves extract toward the mild steel corrosion inhibition remained the same as that of fresh sample. The extract solution kept the same color without any precipitation.

4. CONCLUSIONS

1. Traditional weight loss and electrochemical techniques demonstrated that inhibition efficiency of mild steel in 2M HCl increased as the concentration of Fig leaves extract increased to reach an optimal concentration. Inhibition efficiencies as high as 87% - 90 % were achieved using specific treat rates and under test conditions. Treat rates are to be optimized under real industrial process conditions using reliable monitoring information.
2. EIS results showed that the charge transfer resistance increases and the double layer capacitance decreases.
3. Adsorption of inhibitor molecules on the mild steel surface is found to follow the Langmuir adsorption isotherm at all test temperatures.
4. The activation energy of the corrosion process increases in the presence of Fig leave extract indicating inhibitor physical adsorption.
5. The change in free energy carries negative values around -20 kJ/mole which indicates that the adsorption process is spontaneous and is physical adsorption, respectively.

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