



Tilia Leaves as Eco-Friendly Corrosion Extract for MS in Aqueous Solutions

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ABSTRACT

Tilia Leaves extract investigated as a green corrosion extract for MS (MS) in 1M HCl using mass loss (ML), Tafel polarization (TP), electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods. The obtained results showed that Tilia Leaves extract is an excellent corrosion extract. The inhibition efficiency (ω) increases with increasing the temperature from 25 to 45°C, reaching a maximum value of 79 % at 300 ppm at the temperature of 45°C. Polarization measurements demonstrate that the Tilia Leaves extract acts as a mixed type extract. Nyquist plot illustrates that on increasing Tilia Leaves extract dose, the charge transfer increases (R_{ct}) and the double layer capacitance (C_{dl}) decreases. The adsorption of Tilia Leaves extract on MS obeys Temkin adsorption isotherm.

Keywords: MS, HCl, Corrosion inhibition, Tilia Leaves extract, EIS, EFM.

INTRODUCTION

Iron and its alloys play crucial roles in our daily lives due to their excellent properties, such as high structural and mechanical strengths. MS is the extended metal used in industrial purpose, Army equipment, building and more in manufacturing of installations for petroleum, fertilizers and other industry. So the protection of MS in aqueous solutions is universal request, Economical, environmental, and aesthetical important [1]. The use of extract is more effective way to reduce the corrosion of MS. The organic compounds are widely used as corrosion extracts as it contains heteroatom such as O, N, P, S and heavy metals. But the organic compounds are hazards and unfriendly environment extracts [2]. In spite of the broad spectrum of organic compounds available as corrosion extracts, there is increasing concern about the toxicity of most corrosion extracts because they are toxic to living organism and may also poison the earth [3]. These have prompted searches for green corrosion extracts. According to Eddy et al. [4], green corrosion extracts are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment has been reported by some research groups [5-11]. Tilia Leaves extract are used in the treatment of common cold and bronchitis. This is due to the presence of antinociceptive and anti-inflammatory activities of the two main flavonoid glycosides: kaempferol-3,7-O- α -dirhamnoside and quercetin-3,7-O- α -dirhamnoside which are isolated from the leaves.

The present research will discuss the use of Tilia Leaves extract as green corrosion extract which is renewable source, friendly environmental acceptance, biodegradable, safer and cheaper than other green corrosion extracts for protecting MS in 1M hydrochloric acid. Hydrochloric acid is selected for present study, due to its wide industrial applications such as acid pickling, acid cleaning, water cooling and circulation or acid heat exchanger [12].

MATERIALS AND METHODS

Plant extracts preparation: Tilia Leaves were dried in the shade at room temperature and grind using electrical mill into fine powder then take 1g of powder in 500 mL measuring flask and dissolved in bidistilled water and leave the flask on the hot plate, after that the solution leave to cool at room temperature then filtrate. Take 10 mL filtrate +5 ml ethanol in condensate-collecting flask of rotary evaporator to determined dose of dissolved substance in plant extract solution. The remained weight of dry substance in collection flask after evaporates the solvent equal the equivalent weight dissolved in 10 ml filtrate. By this relation we can prepare stock plant extract solution with desired dose [13].

MS samples: Chemical composition of MS in weight %: C 0.14, Cr 0.10, Ni 0.01, Si 0.024, Mn 0.035, P 0.05, S 0.05 and Fe rest

Test solution: The solution of 1M HCl was prepared for each experiment using analytical grade of hydrochloric acid (37%) and diluted with bidistilled water, its dose was checked by standard solution of Na₂CO₃ solution. The dose range of extract was 50 to 300 ppm

ML measurements: Seven parallel MS sheets of (2×2×0.2) cm were abraded with emery paper (grade 320 to 1200 grit sizes) and then washed with bidistilled water and acetone. After accurate weighting, the specimens were immersed in a 100 mL beaker, which contained 100 mL of HCl with and without addition of different doses of Tilia Leaves. All the aggressive acid solutions were open to air. After 180 min, the sheets were taken out, washed, dried, and weighted accurately. The average ML of seven parallel sheets could be obtained. The % ω and the degree of surface coverage (θ) of Tilia Leaves for the corrosion of MS were calculated as follows [14]:

$$\% \omega = \theta \times 100 = (1 - r^0 / r) \times 100 \quad (1)$$

Where r^0 and r are the values of the average mass loss without and with addition of the extract, respectively

Electrochemical measurements: A three-electrode cell including a working electrode, an auxiliary electrode and a reference electrode was used for the electrochemical measurements. The working electrodes were made of MS sheets which were embedded in PVC holder using epoxy resin with a square surface of 1 cm². The auxiliary electrode was a platinum foil, the reference electrode was a saturated calomel electrode (SCE) with a fine Luggin capillary tube positioned close to the working electrode surface in order to minimize ohmic potential drop (IR). Each specimen was successive abraded by using SiC emery papers up to 1200 grit size, washed with bidistilled water and degreased in acetone then dried between filter papers. The working electrode was immersed in the test solution at open circuit potential for 30 min before measurement until a steady state reached. All the measurements were done in solutions open to atmosphere under unstirred conditions. All potential values were reported versus SCE. Prior to each experiment, the electrode was treated as before. Tafel polarization curves were determined by polarizing to ± 250 mV with respect to the free corrosion potential (E vs. SCE) at a scan rate of 0.5 mV/s. Stern-Geary method [15] used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives $\log i_{\text{corr}}$ and the corresponding corrosion potential (E_{corr}) for extract free acid and for each dose of extract. Then i_{corr} was used for calculation of ω and surface coverage (θ) as in Eq. 2:

$$\% \omega = \theta \times 100 = \left[1 - \left(i_{(inh)} / i_{(free)} \right) \right] \times 100 \quad (2)$$

Where $i_{\text{corr (free)}}$ and $i_{\text{corr(inh)}}$ are the corrosion current densities in the absence and presence of extract, respectively.

EIS measurements were carried out in a frequency range of 100 kHz to 0.1 Hz with amplitude of 5 mV peak-to-peak. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the charge transfer resistance R_{ct} (diameter of high-frequency loop) and the double layer capacity C_{dl} . The ω and the θ obtained from the impedance measurements were calculated from eq. 3:

$$\% \omega = \theta \times 100 = \left(1 - \frac{R_{\text{ct}}^{\circ}}{R_{\text{ct}}} \right) \times 100 \quad (3)$$

Where R_{ct}° and R_{ct} are the charge transfer resistances without and with extract, respectively. EFM tests were carried out using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The higher frequency must be at least two times the lower one. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. The Intermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The large peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_{a} and β_{c}) and the causality factors CF-2& CF-3 [16]. The electrode potential was allowed to stabilize 30 min before starting the measurements.

All the experiments were conducted at 25°C. All electrochemical measurements were performed using Gamry Instrument (PCI4/750) Potentiostat/ Galvanostat / ZRA. This includes a Gamry framework system based on the ESA400. Gamry applications include DC105 software for Tafel polarization, EIS300 software for EIS, and EFM140 software for EFM measurements via computer for collecting data. Echem Analyst 6.03 software was used for plotting, graphing, and fitting data. To test the reliability and reproducibility of the measurements, duplicate experiments, this performed in each case at the same conditions.

RESULTS AND DISCUSSION

Mass loss measurements: Mass loss measurements were carried out for MS in 1M HCl in the absence and presence of different doses of Tilia Leaves are shown in fig.1. The inhibition efficiency (% ω) values calculated are listed in table 1, from this Table, it is noted that the % ω increases steadily with increasing the dose of extract and surface coverage (θ) were calculated by eq.1. The observed inhibition action of the Tilia Leaves could be attributed to the adsorption of its components on MS surface. The formed layer, of the adsorbed molecules, isolates the metal surface from the aggressive medium which limits the dissolution of the latter by blocking of their corrosion sites and hence decreasing the corrosion rate, with increasing efficiency as their doses increase [17].

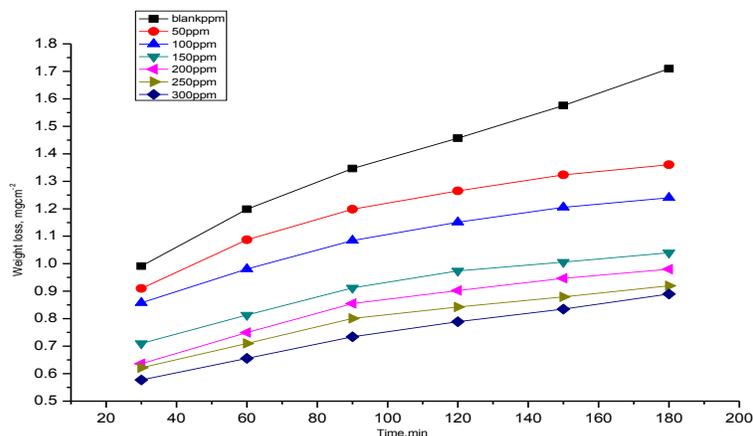


Fig.1. Mass loss-time curves for the corrosion of MS in 1 M HCl without and with different doses of Tilia Leaves at 25°C

Table 1. Corrosion rate (CR) and ω data obtained from mass loss measurements for MS in 1 M HCl solutions without and with various doses of Tilia Leaf extract at 25°C

Conc., ppm	Mass loss mg cm ⁻²	CR, mg cm ⁻² min ⁻¹	θ	% ω
1 M HCl	1.71	0.009	---	----
50	1.36	0.0076	0.205	20.5
100	1.24	0.0069	0.275	27.5
150	1.04	0.0058	0.392	39.2
200	0.98	0.0054	0.427	42.7
250	0.92	0.0051	0.462	46.2
300	0.89	0.0049	0.480	48.0

EIS measurements: The corrosion behavior of MS in 1 M HCl solution in the presence of Tilia Leaves was investigated by EIS at 25°C after 35 min of immersion. Fig.2 shows the results of EIS experiments in the Nyquist representation. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semi-circles, showing that the corrosion process was mainly charge transfer controlled [18]. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole doses, indicating that almost no change in the corrosion mechanism occurred due to the extract addition [19]. The diameter of Nyquist plots (R_p) increases on increasing the Tilia Leaves dose. These results suggest the inhibition behavior of Tilia Leaves on corrosion of MS in 1 M HCl solution. The Nyquist plots are analyzed in terms of the equivalent circuit composed with classic parallel capacitor and resistor (shown in Fig.3.) [20].The impedance of a CPE is described by the equation 4:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (4)$$

Where Y_0 is the magnitude of the CPE, j is an imaginary number, ω is the angular frequency at which the imaginary component of the impedance reaches its maximum values and n is the deviation parameter of the CPE: $-1 \leq n \leq 1$. The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Y_0 and n using equation 5:

$$C_{dl} = Y (\omega_{max})^{n-1} \quad (5)$$

The impedance parameters including charge transfer resistance R_{ct} , double layer capacitance C_{dl} and ω are given in table 2. Also, Bode plots for the MS in 1 M HCl solution are shown in fig.4. In which the high frequency limit corresponding to the electrolyte resistance (ohmic resistance) R_Ω , while the low frequency

represents the sum of ($R_{\Omega} + R_{ct}$), where R_{ct} is in the first approximation determined by both electrolytic conductance of the oxide film and the polarization resistance of the dissolution and repassivation process. At both low and high frequency limits, the phase angle between the current and potential (θ), assumes a value of about 0° , corresponding to the resistive behavior of R_{Ω} and ($R_{\Omega} + R_{ct}$).

Table 2. EIS data of mild steel in 1 M HCl in the presence of different doses of Tilia Leaf extract at 25°C

Conc., ppm	R_{cb} Ωcm^2	$C_{db} \times 10^{-4}$ F cm^{-2}	θ	% ω
1M HCl	129.4	0.689	-----	-----
50	189.5	0.962	0.317	31.7
100	208.7	0.927	0.380	38.0
150	244.3	0.885	0.470	47.0
200	247.5	0.873	0.477	47.7
250	253.1	0.657	0.489	48.9
300	261.0	0.638	0.504	50.4

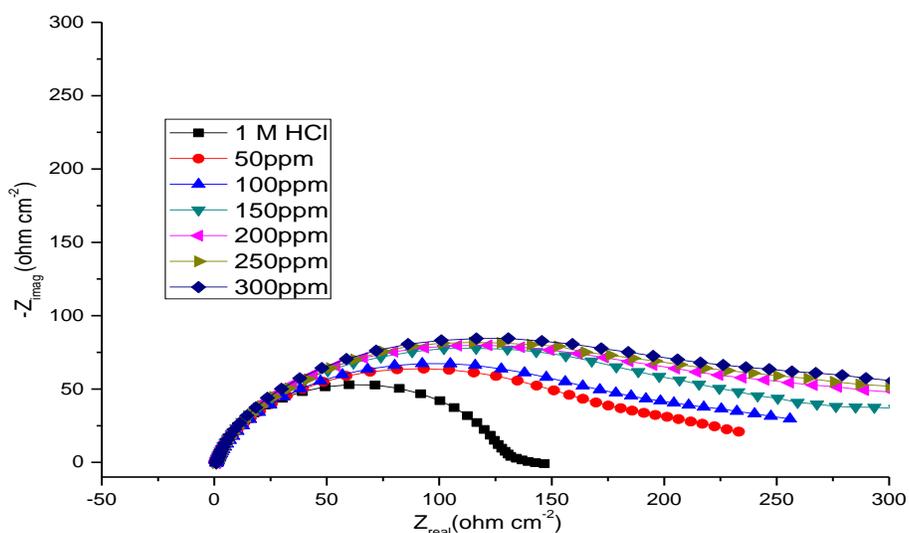


Fig 2. Nyquist plots for MS in 1M HCl at different doses of Tilia Leaves

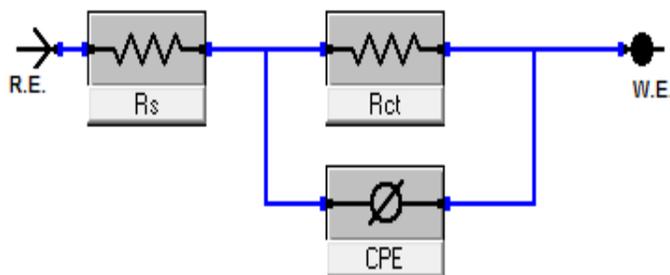


Fig 3. Electrical equivalent circuit used to fit the impedance data

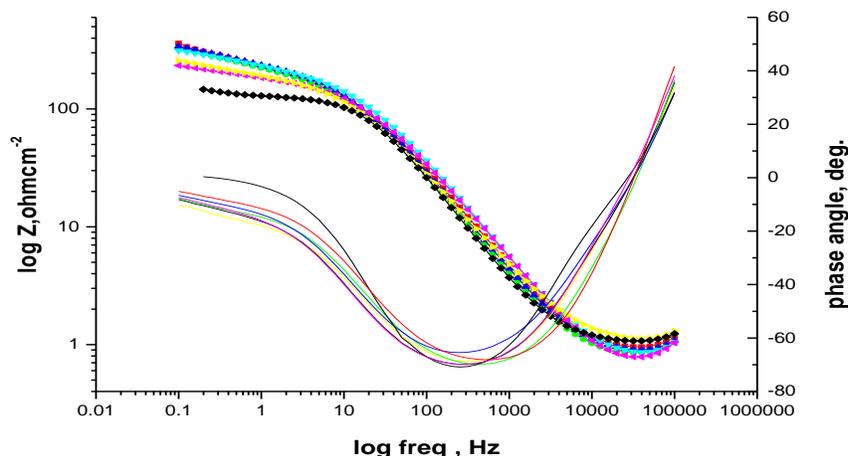


Fig 4. Bode plots for MS in 1M HCl solutions in the absence and presence of various Tilia Leaves doses at 25°C

The main parameters deduced from the analysis of Nyquist diagram are i) the resistance of charge transfer R_{ct} (diameter of high frequency loop) and ii) the capacity of double layer C_{dl} which is defined as :

$$C_{dl} = \frac{1}{2\pi R_{ct} f_{max}} \quad (6)$$

Where f_{max} is the maximum frequency at which the Z_{imag} of the impedance is a maximum. Since the electrochemical theory assumed that $(1/R_{ct})$ is directly proportional to the capacity of double layer C_{dl} , the ω of the extract for MS in 1 M HCl solution was calculated from R_{ct} values obtained from impedance data at different extract doses from equation 3. It is clear that the value of R_{ct} increases on increasing the dose of the extract, indicating that the CR decreases in the presence of the extract. It is also clear that the value of C_{dl} decreases on the addition of extracts, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting the extract molecules function by the formation of the protective layer at the metal surface [21]. Deviations from a perfect circular shape indicate frequency dispersion of interfacial impedance. This anomalous phenomenon is attributed in the literature to the no homogeneity of the electrode surface arising from the surface roughness or interfacial phenomena [22].

Tafel polarization measurements: Figure 5 represents the anodic and cathodic polarization curves of MS electrode, in 1 M HCl solutions containing different doses of Tilia Leaves. Both anodic and cathodic polarization curves are shifted to less current density values in the presence of Tilia Leaves. This behavior suggests the inhibitive action of Tilia Leaves. The extent of the shift in current density increases with increasing of Tilia Leaves dose. The values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel constants (β_a) and cathodic Tafel constant (β_c), excluded from polarization curves are given in table 3.

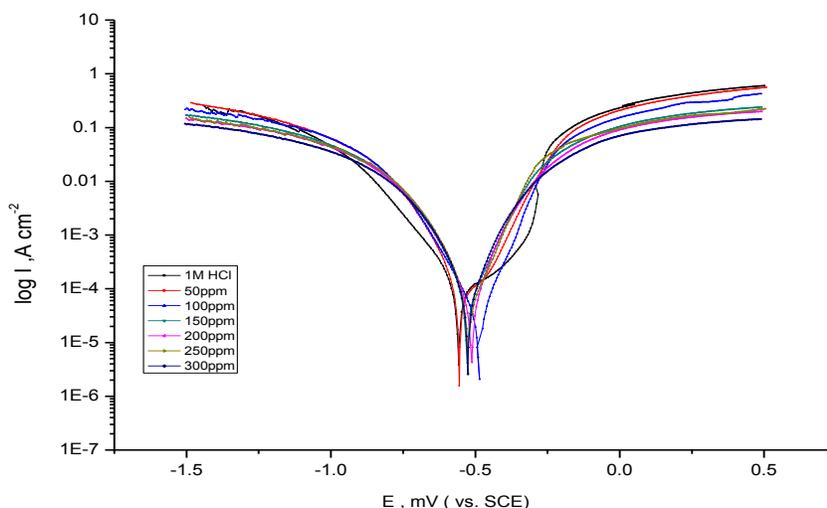


Fig 5. Potentiodynamic plots for corrosion of MS in 1 M HCl without and with different doses of Tilia Leaves at 25°C

Inspection of table 3 reveals that the corrosion potential of MS in the acid solution is largely shifted to less negative values (noble direction) upon addition of Tilia Leaves. On the other hand, the corrosion current density is greatly reduced upon addition of Tilia Leaves. These results suggest the inhibitive effects of the Tilia Leaves. The data in table 3 revealed that the values of ω obtained by polarization technique are comparable to those obtained by ML measurements and EIS. The ω increase with increasing Tilia Leaves dose. Further inspection of table 3 reveals that the addition of increasing doses of Tilia Leaves decreases both the anodic and cathodic Tafel constants. This result indicates that the Tilia Leaves acts as mixed extracts [23]. This means that the Tilia Leaves molecules are adsorbed on both the anodic and cathodic sites resulting in an inhibition of both anodic dissolution and cathodic reduction reactions. The greater the metal surface area occupied by adsorbed molecules, the higher the ω .

Table 3. Potentiodynamic data of mild steel in 1 M HCl with and without different doses of Tilia Leaf extract at 25°C

Conc., ppm	$i_{corr}, \mu A cm^{-2}$	$-E_{corr}, mV vs SCE$	$\beta_a, mVdec^{-1}$	$\beta_c, mVdec^{-1}$	CR, mm^{-1}	θ	% ω
1M HCl	119.0	559	466	108	54.56	---	---
50	80.1	529	106	115	36.61	0.330	33.0
100	72.5	527	96	100	33.13	0.390	39.0
150	61.7	511	98	114	28.21	0.480	48.0
200	57.3	493	101	126	26.19	0.520	52.0
250	49.6	503	97	122	22.68	0.580	58.0
300	44.4	524	119	107	20.27	0.630	63.0

EFM measurements: EFM is a nondestructive corrosion measurement technique that can directly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [24]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Fig.6. shows the frequency spectrum of the current response of MS in 1 M HCl solution, contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The EFM intermodulation spectrums of

MS in 1 M HCl solution containing (50 ppm- 300 ppm) of the Tilia Leaves extract at 25°C is shown in fig.6. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined and are listed in table 4 indicating that this extract inhibits the corrosion of MS in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality [25, 26]. The ω % increases by increasing the studied extract doses and was calculated as in Eq.2.

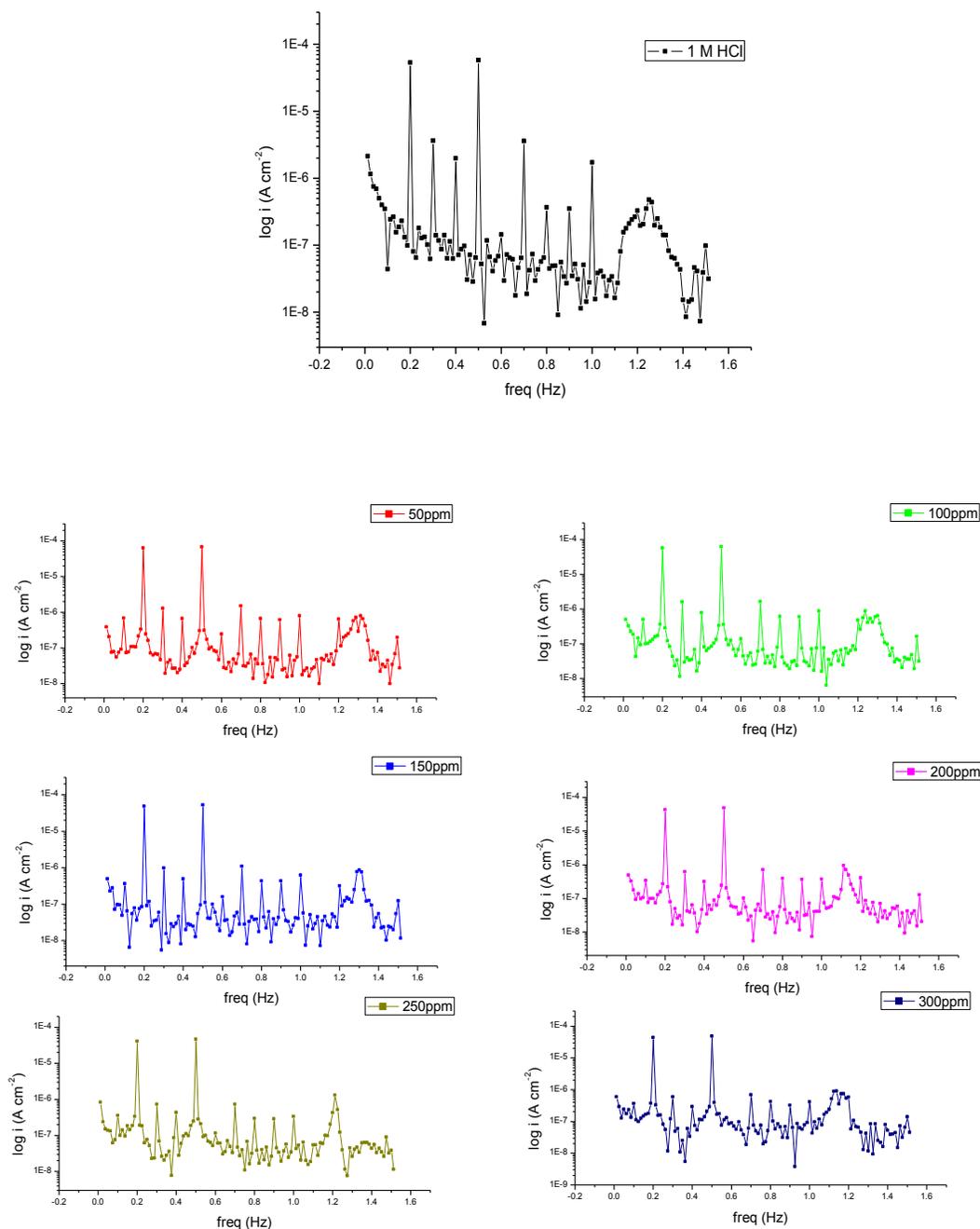
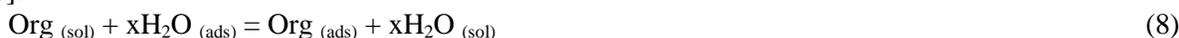


Fig 6. Intermodulation spectrums for the corrosion of MS in 1 M HCl without and with various doses of Tilia Leaves at 25°C

Table 4. Electrochemical kinetic parameters obtained by EFM technique for MS without and with of various doses of the Tilia Leaf extract in 1 M HCl at 25°C

Conc., ppm	i_{corr} , $\mu A cm^{-2}$	β_a , $mV dec^{-1}$	β_c , $mV dec^{-1}$	C.R. mpy	CF-2	CF-3	θ	% ω
0.0	171.6	143	332	78.41	1.9	2.2	----	---
50	116.1	108	126	53.03	1.9	3.4	0.323	32.3
100	112	111	136	51.2	1.8	3.6	0.347	34.7
150	103.9	123	145	47.48	1.9	3.29	0.395	39.5
200	91.09	121	136	41.62	1.85	2.77	0.469	46.9
250	88.7	123	141	40.53	1.9	2.95	0.483	48.3
300	85.74	127	127	39.18	1.95	3.6	0.500	50.0

Adsorption isotherms: Basic information on the interaction between extracts and metal surface can be provided using the adsorption isotherms [27]. The adsorption of an organic molecules at metal–solution interface can occur as a result of substitution adsorption process between organic molecules presented in the aqueous solution (Org), and the water molecules previously adsorbed on the metallic surface (H_2O) [28]:



Where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively H_2O is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic molecule. The surface coverage values (θ) were evaluated using corrosion rate values obtained from the mass loss method. The (θ) values for different extract doses were tested by fitting to various isotherms. The best fit was obtained with Temkin adsorption isotherm (Fig. 7), given by Eq. (9) [29].

$$\theta = 1/f \ln K_{ads} C \quad (9)$$

Where f is the heterogeneous factor of the metal surface describing the molecular interactions in the adsorbed layer [30]. If $f > 0$, mutual repulsion of molecules occurs and if $f < 0$ attraction takes place [31]. In fig.7 it can be seen that the linear correlation coefficient (R^2) is close to 1 and the slope of straight line is also close to 1, which suggests that the adsorption of Tilia Leaves from 1 M HCl solution on MS obeys the Temkin model and exhibit single-layer adsorption characteristic. From the intercept of the straight line K_{ads} value can be calculated. The equilibrium constant of the adsorption process K_{ads} , is related to the standard free energy of adsorption, ΔG_{ads}° , from the following equation [32]:

$$K_{ads} = 1/55.5 \exp(\Delta G_{ads}^{\circ}/RT) \quad (10)$$

The value 55.5 is the dose of water in solution in $mol l^{-1}$. The calculated ΔG_{ads}° values, using Eq. 10 was also given in table 5.

Table 5. Values of adsorption isotherm parameters for MS in 1 M HCl contain different doses of Tilia Leaf extract

Temp., K	Adsorption isotherm	K_{ads} , $g^{-1}L$	$-\Delta G_{ads}^{\circ}$, $kJ mol^{-1}$
298	Temkin	904.9	26.8
303		1400.5	28.4
308		1729.9	29.4
313		6847.5	33.4
315		151444.7	42.2

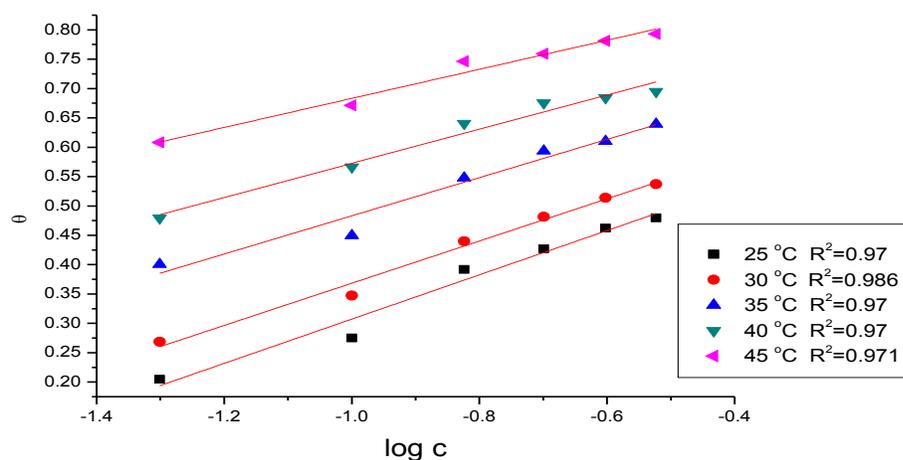


Fig.7. Temkin adsorption plots for MS in 1 M HCl containing various doses of Tilia Leaves at 25°C

The negative values of $\Delta G_{\text{ads}}^{\circ}$ ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the steel surface. Early speaking, the adsorption type is regarded as physisorption if the value of $\Delta G_{\text{ads}}^{\circ}$ was of the order of 20 kJ mol⁻¹ or lowers. The inhibition behavior is attributed to the electrostatic interaction between the organic molecules and iron atom. With the value of $\Delta G_{\text{ads}}^{\circ}$ is of the order of 40 kJ mol⁻¹ or higher, the adsorption could be seen as chemisorption. In this process, the covalent bond is formed by the charge sharing or transferring from the extract molecules to the metal surface [33, 34]. Based on the literature [35], the calculated $\Delta G_{\text{ads}}^{\circ}$ values in this work (Table 5) indicate that the adsorption mechanism of Tilia Leaves on MS in 1 M HCl solution is typically chemisorption. The same conclusion was given by Wang et al. [36] and Hassan [37]. The large negative value of $\Delta G_{\text{ads}}^{\circ}$ of Tilia Leaves indicates that this extract is strongly adsorbed on the steel surface [38,39].

Effect of temperature: The effect of temperature on the corrosion rate of MS in free acid and in the presence of different doses of Tilia Leaves was studied in the temperature range of 25–45°C using mass loss measurements. The CR values of MS with and without the addition of Tilia Leaves extract in 1 M HCl at various temperatures are listed in table 6. These data showed that the corrosion rate values decreased as the dose and temperature of the Tilia Leaves increased and hence the corrosion ω increased. This behavior was observed for chemisorption of extracts on metal surfaces. Fig.8. represents Arrhenius plot (as log k versus 1/T) for MS corrosion in 1M HCl in the absence and presence of various doses of Tilia Leaves. Straight lines were obtained with slope equals to $E_a^* = 2.303 R$. The values of E_a^* for the corrosion reaction in the absence and presence of Tilia Leaves were calculated and are presented in table 6. In examining the effect of temperature on the corrosion process in the presence of the Tilia Leaves, the Arrhenius equation below was used:

$$\text{Log } k = -E_a^* / 2.303RT + \text{log } A \quad (11)$$

Where k is the corrosion rate, E_a^* is the apparent activation energy, and A is the frequency factor.

Table7 shows the decrease of E_a^* decelerated the corrosion rate of steel. E_a^* values of the corrosion process of protected MS are lower than the unprotected MS in 1 M HCl solution. The large decrease in the activation energy of the corrosion process in the presence of the extract indicates the higher ω of the extract. The decrease of the activation energy is due to the adsorption of extract molecules on the metal surface to form stable metal-extract complex (M-Inh) [40].

The other thermodynamic parameters (ΔS^* and ΔH^*) were calculated from the linear regression of transition state (Fig.9.) using Eq. (12).

$$k = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (12)$$

Where k is rate of corrosion, h is Planck's constant, N is Avogadro number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. A plot of $\log(k/T)$ vs. $1/T$ (Fig. 9.) should give a straight line, with a slope of $(\Delta H^*/2.303R)$ and an intercept of $[\log(R/Nh)+\Delta S^*/2.303R]$ Examination of the kinetic values shows that the increase of extract dose leads to increases of all parameters of corrosion process (Table 7). The positive value of the enthalpy ΔH^* means that the process is endothermic and it needs more energy to achieve the activated state or equilibrium [41, 42]. The negative value of ΔS^* (Table7) for Tilia Leaves indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of transition from reactant to the activated complex [43].

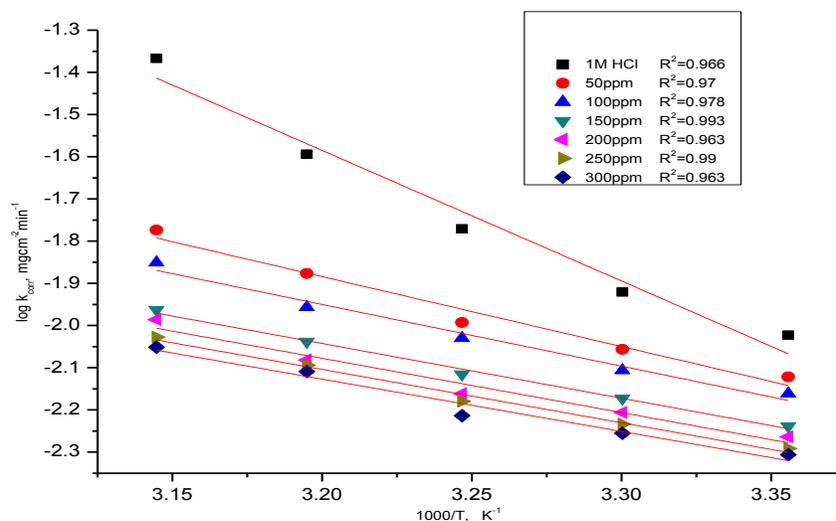


Fig 8. Log k (corrosion rate) – $1/T$ curves for MS in 1 M HCl in the absence and presence of different doses of Tilia Leaves extract

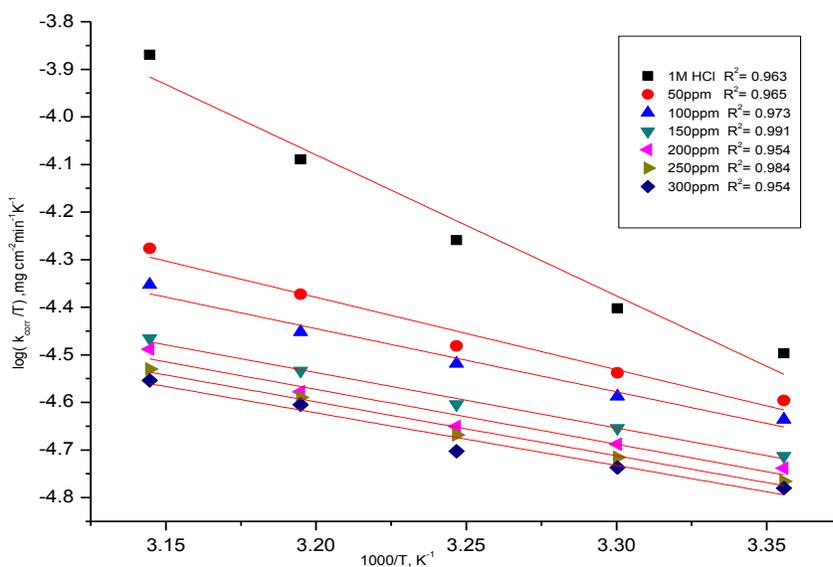


Fig 9. Log k (corrosion rate)/ T – $1/T$ curves for MS in 1 M HCl in the absence and presence of different doses of Tilia Leaves extract

Table 6. Data of weight loss measurements for MS in 1 M HCl solution in the absence and presence of different doses of Tilia Leaf extract at different temperatures

Conc., ppm	Temp., °C	C.R., mg cm ⁻² min ⁻¹	θ	% ω
50	25	0.0076	0.205	20.5
	30	0.0088	0.269	26.9
	35	0.0102	0.4	40.0
	40	0.0133	0.479	47.9
	45	0.0168	0.608	60.8
100	25	0.0069	0.275	27.5
	30	0.0078	0.437	43.7
	35	0.0093	0.45	45.0
	40	0.0111	0.566	56.6
	45	0.0141	0.671	67.1
150	25	0.0058	0.392	39.2
	30	0.0067	0.44	44.0
	35	0.0077	0.548	54.8
	40	0.0092	0.641	64.1
	45	0.0109	0.746	74.6
200	25	0.0054	0.427	42.7
	30	0.0062	0.481	48.1
	35	0.0069	0.594	59.4
	40	0.0083	0.675	67.5
	45	0.0103	0.759	75.9
250	25	0.0051	0.462	46.2
	30	0.0058	0.514	51.4
	35	0.0066	0.61	61.0
	40	0.0081	0.684	68.4
	45	0.0094	0.781	78.1
300	25	0.0049	0.488	48.8
	30	0.0056	0.537	53.7
	35	0.0061	0.64	64.0
	40	0.0078	0.695	69.5
	45	0.0089	0.793	79.3

Table 7. Activation parameters for dissolution of MS in the absence and presence of different doses of Tilia Leaf extract in 1 M HCl at different temperatures

Conc., ppm	E_a , kJ mol ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹
1M HCl	59.3	24.6	94.2
50	31.7	12.7	188.2
100	28.0	11.0	201.4
150	24.8	9.7	213.2
200	24.6	9.6	214.5
250	24.2	9.4	216.3
300	23.7	9.2	218.3

Mechanism of corrosion inhibition process: Plant products are organic in nature, containing constituents such as tannins, organic and amino acids, alkaloids and pigments that are known to exhibit inhibiting action [44]. Preliminary phytochemical investigation in the literature showed that Tilia Leaf extract contains two main flavonoid glycosides: kaempferol-3,7-*O*- α -dirhamnoside and quercetin-3,7-*O*- α -dirhamnoside. It is therefore appropriate to say that the adsorption of these compounds onto metal surface

is responsible for corrosion inhibition effect and hence difficult to assign the inhibitive effect to a particular constituent.

CONCLUSIONS

On the basis of this study the following conclusions can be drawn:

i) Tilia Leaves act as extract for MS corrosion in acidic medium (ii) ω of Tilia Leaves increases with increase in dose of the extract and also with increase in temperature (iii) The corrosion inhibition is probably due to the adsorption of the Tilia Leaves on the metal surface and blocking its active sites by phenomenon of chemical adsorption. (vi) Tilia Leaves was found to obey Temkin adsorption isotherm from the fit of the experimental data at all the doses studied (v) The values of E_a^* obtained in the presence of the Tilia Leaves were lower compared to the blank acid solution which further support the chemical adsorption proposed (vii) The values of ΔG_{ads}^0 obtained are low and negative, which reveals the spontaneity of the adsorption process and (viii) The results indicate that, the Tilia Leaves acts as mixed type extract.

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