Abd El-Aziz S.Fouda[1], Samir A. Abd El-Maksoud[2],
Hosam M.Mostafa[1]*

[1]*Mansoura University, Department of Chemistry, Faculty of Science,
Mansoura, Egypt, [2]Port Said University, Department of Chemistry,
Faculty of Science,Port Said, Egypt*

Tilia leafs as eco-friendly corrosion inhibitor for mild steel in aqueous solutions

ABSTRACT

Tilia Leafs extract activity as a green corrosion inhibitor (environmental friendly) for mild steel in 1M HCl has been tested using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). The obtained results show that Tilia Leafs extract is an excellent corrosion inhibitor. The inhibition efficiency increases with increasing the temperature from 25 to 45°C, reaching a maximum value of 79 % at the highest concentration of 300 ppm at the temperature of 45°C. Polarization measurements demonstrate that the Tilia Leafs extract acts as a mixed type inhibitor. Nyquist plot illustrates that on increasing Tilia Leafs extract concentration, the charge transfer increases and the double layer capacitance decreases. The adsorption of Tilia Leafs extract on mild steel obeys Temkin adsorption isotherm.
Keywords: *Mild steel, HCl, Corrosion inhibition, Tilia Leafs extract, EIS.*

1. INTRODUCTION

Iron and its alloys play crucial roles in our daily lives due to their excellent properties, such as high structural and mechanical strengths. Mild steel 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 mild steel in aqueous solutions is universal request, Economical, environmental, and aesthetical important [1]. The use of inhibitor is more effective way to reduce the corrosion of mild steel. The organic compounds are widely used as corrosion inhibitors as it contains heteroatom such as O, N, P, S, and heavy metals. But the organic compounds are hazards and unfriendly environment inhibitors [2]. In spite of the broad spectrum of organic compounds available as corrosion inhibitors, there is increasing concern about the toxicity of most corrosion inhibitors because they are toxic to living organism and may also poison the earth [3]. These have prompted searches for green corrosion inhibitors.

According to Eddy et al. [4], green corrosion inhibitors 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].

The present research will discuss the use of Tilia Leafs extract as green corrosion inhibitor which is renewable source, friendly environmental acceptance, biodegradable, safer and cheaper than other green corrosion inhibitors for protecting mild steel 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].

2. EXPERIMENTAL METHODS

Mild steel samples

Chemical composition of mild steel 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 distilled water, its concentration was checked by standard solution of

Na_2CO_3 solution. The concentration range of inhibitor was in the range 50 to 300 ppm

Plant extract preparation

Tilia Leafs were dried in the shade at room temperature and grind using electrical mill into fine powder then take one gram 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 concentration 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 concentration [13].

Weight lose measurements

Seven parallel mild steel sheets of (2×2×0.2) cm were abraded with emery paper (grade 320 to1200 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 Leafs. All the aggressive acid solutions were open to air. After 180 minutes, the specimens were taken out, washed, dried, and weighted accurately. The average weight loss of seven parallel mild steel sheets could be obtained. The inhibition efficiency (%IE) and the degree of surface coverage of Tilia Leafs for the corrosion of mild steel were calculated as follows [22]:

$$\%IE = \theta \times 100 = [1 - (W/W^o)] \times 100 \qquad (1)$$

Where W^o and W are the values of the average weight loss without and with addition of the extract, respectively

Electrochemical measurement

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 mild steel sheets which were embedded in PVC holder using epoxy resin with a square surface of 1 cm^2.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 [14] used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives log i_{corr} and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each dose of inhibitor. Then i_{corr} was used for calculation of inhibition efficiency (% IE) and surface coverage (θ) as in equation 2:

$$\% IE = \theta \times 100 = [1 - (i_{(inh)} / i_{(free)})] \times 100 \qquad (2)$$

Where $i_{corr\,(free)}$ and $i_{corr\,(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, 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 inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are calculated from equation 3:

$$\%IE = \theta \times 100 = [1 - (R^o_{ct}/R_{ct})] \times 100 \qquad (3)$$

Where R^o_{ct} and R_{ct} are the charge transfer resistance 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 [24]. 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 potentiodynamic 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.

3. RESULTS AND DISCUSSION

Weight loss measurements

Weight loss measurements were carried out for mild steel in 1M HCl in the absence and presence of different doses of Tilia Leafs are shown in Figure (1).

The inhibition eficiency (% IE) values calculated are listed in Table 1, from this table, it is noted that the %IE increases steadily with increasing the dose of inhibitor and surface coverage ( ) were calculated by equation (1).

The observed inhibition action of the Tilia Leafs could be attributed to the adsorption of its components on mild steel 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 [16].

Table 1. Corrosion rate (C.R.) and inhibition efficiency data obtained from weight loss measurements for mild steel in 1 M HCl solutions without and with various doses of Tilia Leaf extract at 25°C and 120 min immersion

Tabela 1. Podaci o stepenu korozije (C.R.) i efikasnosti inhibicije dobijeni iz mjerenja gubitaka težine za meki elik u 1M HCl rastvorima bez i sa razli itim koncentra-cijama ekstrakta Tilia Leafa na 25°C

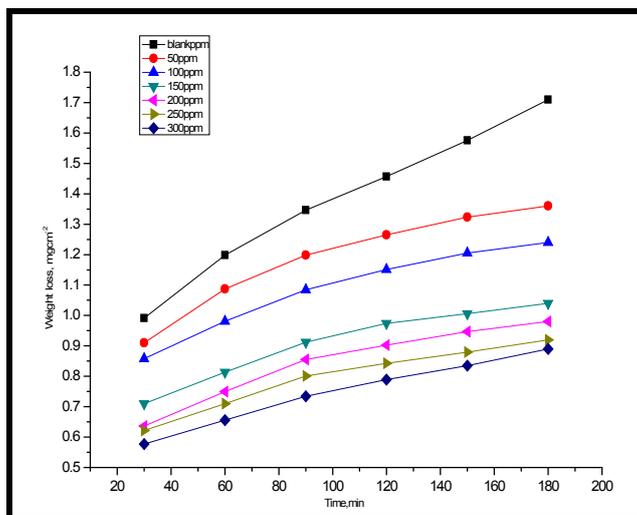| Conc., ppm	Weight loss, mg cm^{-2}	C.R., mg cm^{-2} min^{-1}		% IE
1 M HCl	1.71	0.009	---	----
50	1.36	0.0076	0.205	20.5
100	1.24	0.0069	0.275	27.5
150	1.04	0.0058	0.392	39.2
200	0.98	0.0054	0.427	42.7
250	0.92	0.0051	0.462	46.2
300	0.89	0.0049	0.480	48.0

Figure 1. Weight loss-time curves for the corrosion of mild steel in 1 M HCl in the absence and presence of different doses of Tilia Leafs at 25°C
Slika 1. Kriva gubitka težine za koroziju mekog elika u 1M HCl u odsustvu i prisustvu razli itih koncentracija Tilia Leafs inhibitora na 25°C

EIS measurements

The corrosion behavior of mild steel in 1M HCl solution in the presence of Tilia Leafs was investigated by EIS at 25°C after 30 min of immersion. Figure 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 semicircles, showing that the corrosion process was mainly charge transfer controlled [17]. 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 inhibitor addition [18]. The diameter of Nyquist plots (R$_p$) increases on increasing the Tilia Leafs dose. These results suggest the inhibition behavior of Tilia Leafs on corrosion of mild steel in 1M HCl solution.
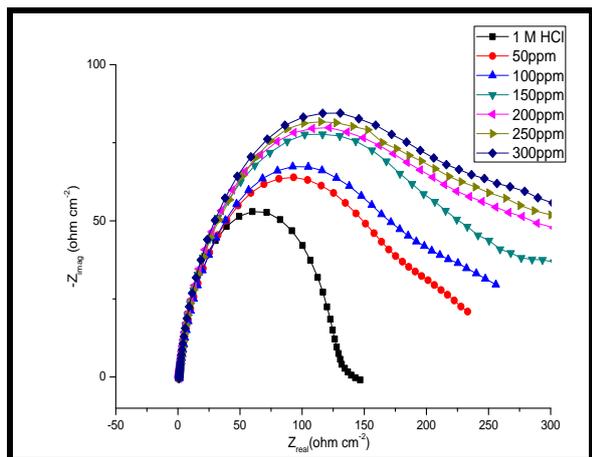
Figure 2. Nyquist plots for mild steel in 1M HCl at different doses of Tilia Leafs

Slika 2. Nyquist-ove krive za meki čelik u 1M HCl pri različitim koncentracijama Tilia Leafs inhibitora

The Nyquist plots are analyzed in terms of the equivalent circuit composed with classic parallel capacitor and resistor, Figure 3 [19]. The impedance of a CPE is described by the equation 4:

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

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:

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

The impedance parameters including polarization resistance R_{ct}, double layer capacitance C_{dl} and inhibition efficiency % IE are given in Table 2.

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

Tabela 2. EIS mekog čelika u 1M HCl u prisustvu različitih koncentracija ekstrakta Tilia Leafa na 25^oC

Conc., ppm	R_{ct}, cm^2	C_{dl}, x10^{-4} F cm^{-2}		% IE
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

Also, Bode plots for the mild steel in 1M HCl solution are shown in Figure 4. In which the high frequency limit corresponding to the electrolyte resistance (ohmic resistance) R, while the low frequency represents the sum of (R + 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 ( ), assumes a value of about 0°, corresponding to the resistive behavior of R and (R + R_{ct}).
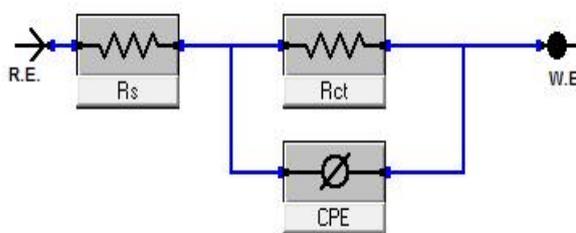

Figure 3. Electrical equivalent circuit used to fit the impedance data

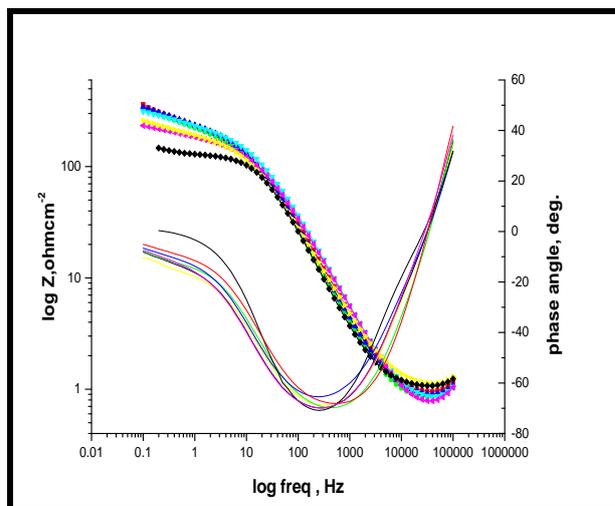*Slika 3. Električno ekvivalentno kolo koje se koristi za određivanje impedance*

Figure 4. Bode plots for mild steel in 1M HCl solutions in the absence and presence of various Tilia Leafs doses at 25^oC

Slika 4. Krive za meki čelik u 1M HCl rastvoru u odsustvu i prisustvu različitih koncentracija Tilia Leafs inhibitora na 25^oC

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

$$C_{dl} = \frac{1}{2\pi R_{ct} f_{max}}$$

(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 inhibition efficiency (%IE) of the inhibitor for Carbon steel in 1M HCl solution was calculated from R_{ct} values obtained from impedance data at different inhibitor doses from the equation3

It is clear that the value of R_{ct} increases on increasing the dose of the inhibitor, indicating that the corrosion rate decreases in the presence of the inhibitor. It is also clear that the value of C_{dl} decreases on the addition of inhibitors, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting the inhibitor molecules function by the formation of the protective layer at the metal surface [20]. 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 [21,22].

Tafel polarization measurements

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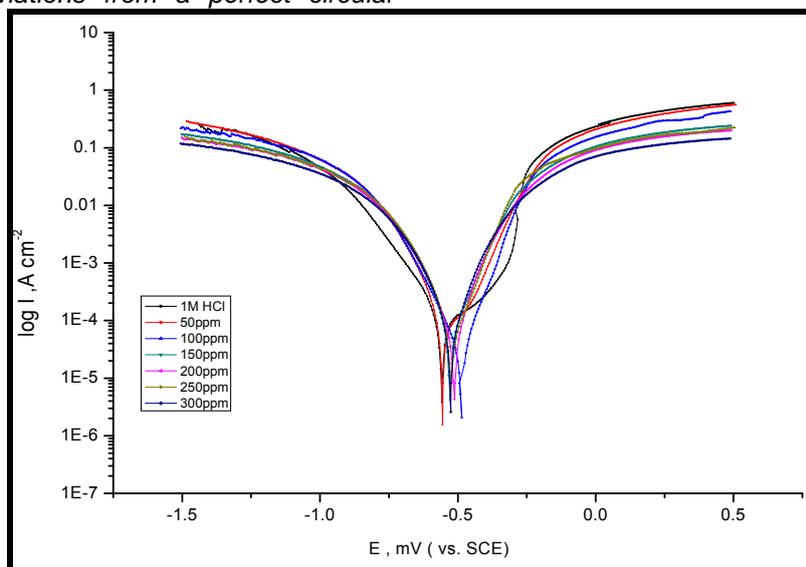

Figure 5. Potentiodynamic plots for corrosion of mild steel in 1 M HCl in the absence and presence of different doses of Tilia Leafs at 25°C
Slika 5. Potentiodinami ke krive za koroziju mekog elika u 1M HCl u odsustvu i prisustvu razli itih koli ina Tilia Leafs inhibitora na 25°C

Inspection of Table 3 reveals that the corrosion potential of Carbon steel in the acid solution is largely shifted to less negative values (noble direction) upon addition of Tilia Leafs. On the other hand, the corrosion current density is greatly reduced upon addition of Tilia Leafs. These results suggest the inhibitive effects of the Tilia Leafs.

The data in Table 3 reveal that the values of inhibition efficiency obtained by polarization technique are comparable to those obtained by weight loss measurements and EIS. The inhibition

efficiency increases with increasing Tilia Leafs concentration. Further inspection of Table 3 reveals that the addition of increasing doses of Tilia Leafs decreases both the anodic and cathodic Tafel constants. This result indicates that the Tilia Leafs acts as mixed inhibitors [23]. This means that the Tilia Leafs 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 inhibition efficiency.

Table 3. Potentiodynamic data of mild steel in 1 M HCl in the presence of different doses of Tilia Leaf extract at 25^oC

Tabela 3. Potentiodinami ki podaci mekog elika u 1M HCl u prisustvu razli itih koncentracija ekstrakta Tilia Leafa na 25^oC

Conc., ppm	i_{corr}, $\mu A\ cm^{-2}$	$-E_{corr}$, mV vs SCE	$_a$, $mVdec^{-1}$	$_c$, $mVdec^{-1}$	CR, mmy^{-1}		%IE
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 measure-ment 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. Figure 6 shows the frequency spectrum of the current response of mild steel in 1M 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 mild steel in 1M HCl solution containing (50 ppm- 300 ppm) of the Tilia Leafs extract at $25^°C$ is shown in Figure 6. The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [25]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes ($_c$ and $_a$) and the causality factors (CF-2 and CF-3).

Table 4. Electrochemical kinetic parameters obtained by EFM technique for mild steel in the absence and presence of various doses of the Tilia Leaf extract in 1 M HCl at 25ºC

Tabela 4. Elektrohemijski kineti ki parametri dobijeni EFM tehnikom za meki elik u odsustvu i prisustvu razli itih koncentracija ekstrakta Tilia Leaf u 1M HCl na 25ºC

Conc., ppm	i_{corr}, $\mu A\ cm^{-2}$	$_a$ mV dec^{-1}	$_c$ mV dec^{-1}	C.R. mpy	CF-2	CF-3		%IE
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	112.0	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	91.1	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	85.7	127	127	39.18	1.95	3.6	0.500	50.0

These electrochemical parameters were simultaneously determined by Gamry EFM140 software, and listed in Table 4 indicating that this extract inhibits the corrosion of mild steel in 1M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2&3) indicating that the measured data are verified and of good quality [26]. The inhibition efficiencies IE_{EFM} % increase by increasing the studied extract doses and was calculated as in Eq. 2.
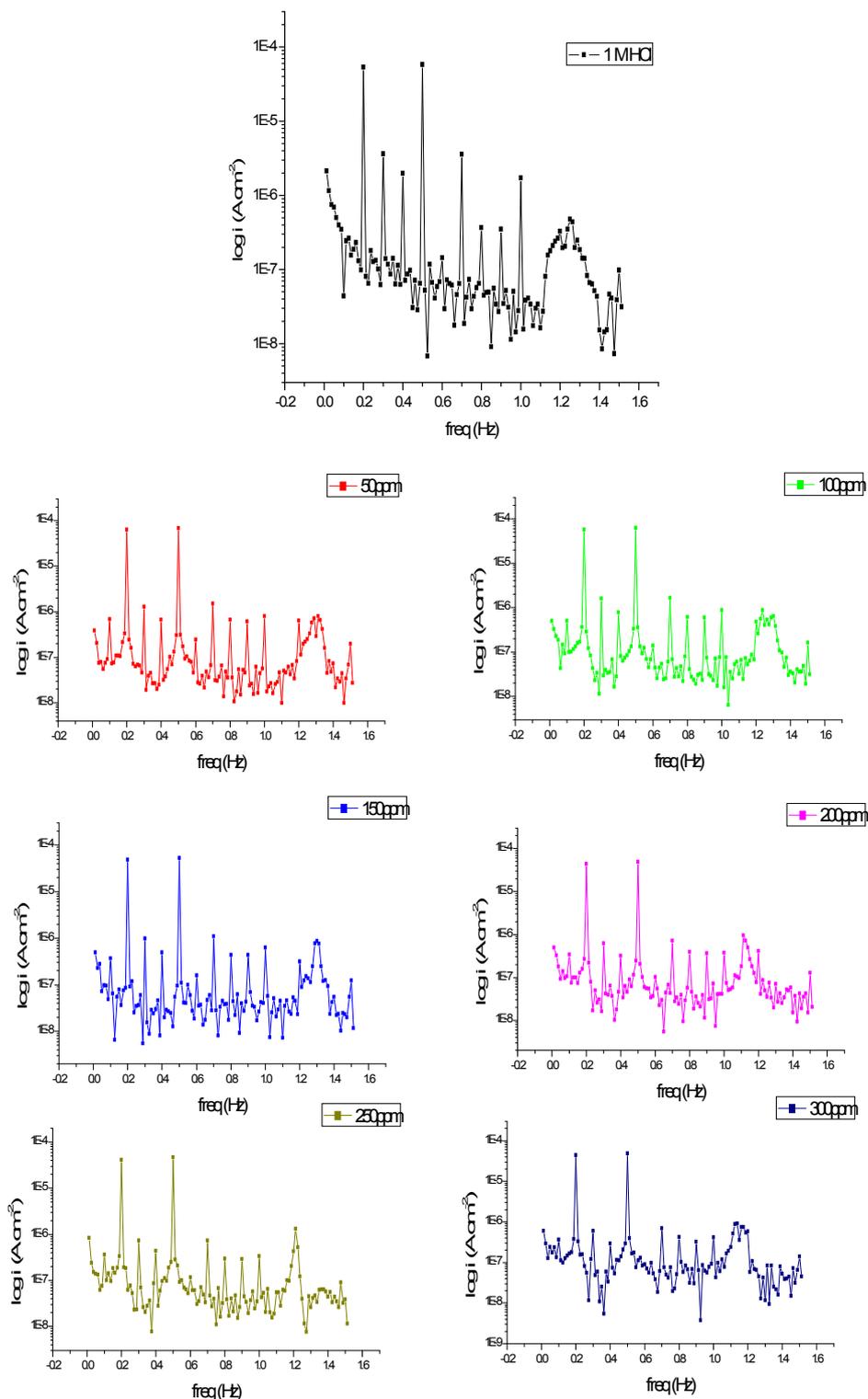
Figure 6. Intermodulation spectrums for the corrosion of mild steel in 1M HCl without and with various doses of Tilia Leafs at 25°C
*Slika 6. Intermodulacijski spektri za koroziju mekog čelika u 1M HCl bez i sa različitim koncentracijama Tilia Leafs inhibitora na 25°C*

Adsorption isotherms

Basic information on the interaction between inhibitors 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]:

$$Org_{(sol)} + xH_2O_{(ads)} = Org_{(ads)} + xH_2O_{(sol} \quad (7)$$
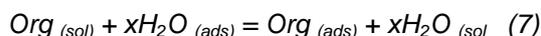
Where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively H_2O is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic molecule. The surface coverage values ( ) were evaluated using corrosion rate values obtained from the weight loss method. The ( ) values for different inhibitor doses were tested by fitting to various isotherms. The best fit was obtained with Temkin adsorption isotherm (Fig. 7), given by Eq. (8) [29].

$$ = 1/f \ln K_{ads}C \quad (8)$$

Where f is the heterogeneous factor of the metal surface describing the molecular interactions in the adsorption layer [30]. If f > 0, mutual repulsion of molecules occurs and if f < 0 attraction takes place [31]. In Figure 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 Leafs from 1M HCl solution on mild steel 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, $G°_{ads}$, from the following equation [32]:

$$K_{ads}=1/55.5 \exp (G^0_{ads}/RT) \quad (9)$$

The value 55.5 is the concentration of water in solution in mol l^{-1}. The calculated G^0_{ads} values, using Eq. (10), were also given in Table 5.
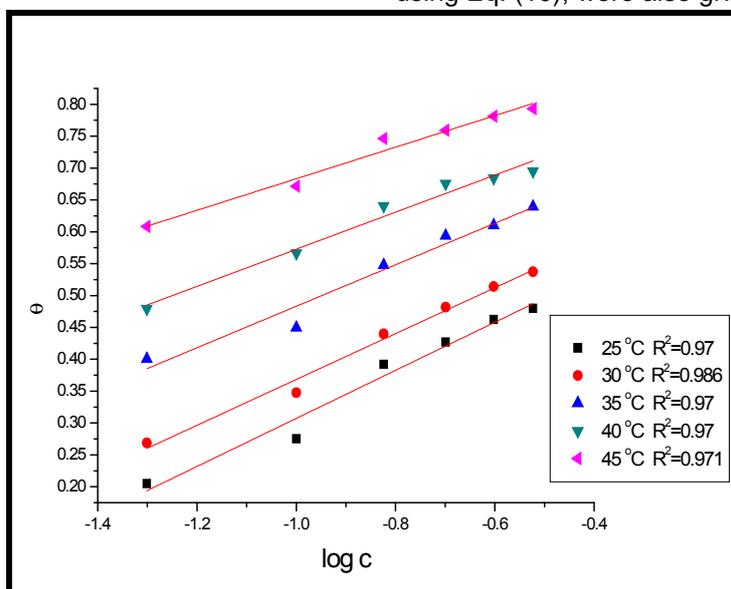

Figure 7. Temkin adsorption plots for mild steel in 1M HCl containing various doses of Tilia Leafs at 25°C

Slika 7. Temkinove adsorpcione krive za meki čelik u 1M HCl sa različitim koncentracijama Tilia Leafs inhibitora na 25°C

The negative values of $G°_{ads}$ 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 absolute value of G^0_{ads} 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 absolute value of $G°_{ads}$ 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 inhibitor molecules to the metal surface [33, 34].

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

Tabela 5. Vrednosti parametara izoterme adsorpcije za meki čelik u 1M HCl pri različitim koncentracijama ekstrakta Tilia Leaf

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

Based on the literature [35], the calculated G^o_{ads} values in this work, Table 5 indicate that the adsorption mechanism of Tilia Leafs on mild steel in 1M HCl solution is typically chemisorption. The same conclusion was given by Wang et al. [36] and Hassan [37] .The large negative value of G^0_{ads} of Tilia Leafs indicates that this extract is strongly adsorbed on the steel surface [47-48].

Effect of temperature

The effect of temperature on the corrosion rate of mild steel in free acid and in the presence of different doses of Tilia Leafs was studied in the temperature range of 25–45°C using weight loss measurements. The corrosion rate values of mild steel with and without the addition of Tilia Leafs extract in 1M HCl at various temperatures are listed in Table 6.

Table 6. Data of weight loss measurements for mild steel in 1 M HCl solution in the absence and presence of different doses of Tilia Leaf extract at different temperatures after 120 min immersion

Tabela 6. Podaci o merenjima gubitka težine za meki elik u 1M HCl rastvoru u odsustvu i prisustvu razli itih koncentracija ekstrakta Tilia Leafa na razli itim temperaturama

Conc., ppm	Temp., ^{o}C	C.R., mg cm^{-2} min^{-1}		% IE
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

These data showed that the corrosion rate values decreased as the concentration and temperature of the Tilia Leafs increased and hence the corrosion inhibition efficiency increased. This behavior was observed for chemisorption of inhibitors on metal surfaces.

Figure 8 represents Arrhenius plot (as log k versus 1/T) for mild steel corrosion in 1M HCl in the absence and presence of various doses of Tilia Leafs. 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 Leafs were calculated and are presented in Table 6. In examining the effect of temperature on the corrosion process in the presence of the Tilia Leafs, the Arrhenius equation below was used:

$$Log\ k = -E^*_a/2.303RT + log\ A \qquad (10)$$

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

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

Tabela 7. Parametri aktivacije za rastvaranje mekog elika u odsustvu i prisustvu razli itih koncentracija ekstrakta Tilia Leaf u 1M HCl na razli itim temperaturama

Conc., ppm	E^*_a kJ mol^{-1}	H^*, kJ mol^{-1}	- S^*, 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

Table 7 shows the decrease of E^*_a decelerated the corrosion rate of steel. E^*_a values of the corrosion process of protected mild steel are lower than the unprotected mild steel in 1M HCl solution. The large decrease in the activation energy of the corrosion process in the presence of the inhibitor indicates the higher inhibition efficiency of the inhibitor. The decrease of the activation energy is due to the adsorption of inhibitor molecules on the metal surface to form stable metal-inhibitor complex (M- Inh) [40].
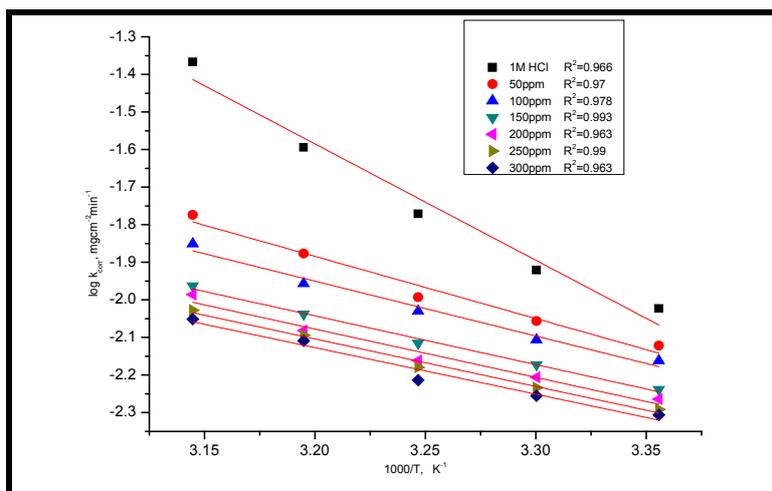
Figure 8. Log k (corrosion rate) – 1/T curves for mild steel in 1 M HCl in the absence and presence of different doses of Tilia Leafs extract

Slika 8. Log k (brzina korozije) - 1/T krive za meki čelik u 1M HCl u odsustvu i prisustvu različitih koncentracija ekstrakta Tilia Leafs inhibitora

The other thermodynamic parameters (ΔS^* and ΔH^*) were calculated from the linear regression of transition state (Fig.9) using Eq. (11)

$$k = (RT/Nh)\ exp^{(\Delta S^*/R)}\ exp^{(-\Delta H^*/RT)} \qquad (11)$$

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, Figure 8 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 [50-51].The negative value of ΔS^*, Table7 for Tilia Leafs 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].
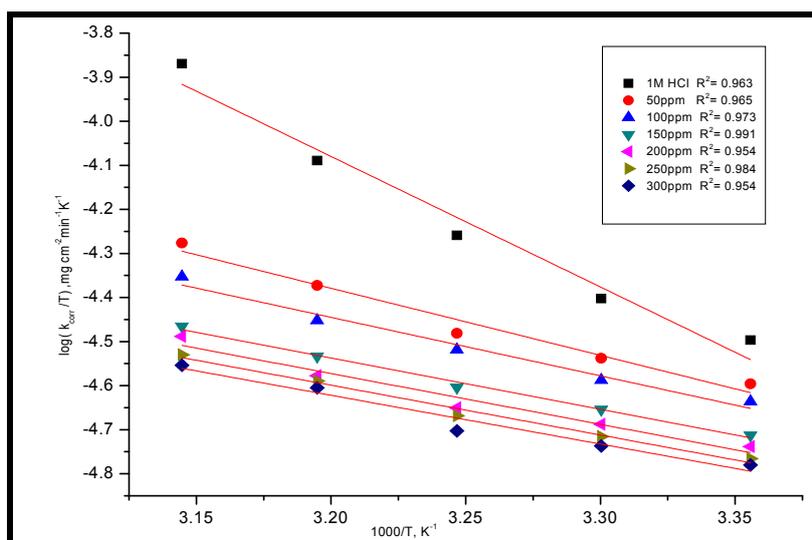

Figure 9. Log k (corrosion rate)/T – 1/T curves for mild steel in 1 M HCl in the absence and presence of different doses of Tilia Leafs extract

Slika 9. Log k (brzina korozije) / T - 1 / T krive za meki čelik u 1M HCl u odsustvu i prisustvu različitih koncentracija ekstrakta Tilia Leafs inhibitora

4. CONCLUSIONS

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

(1) Tilia Leafs act as inhibitor for mild steel corrosion in acidic medium.

(2) Inhibition efficiency of Tilia Leafs increases with increase in dose of the extract and also with increase in temperature.

(3) The corrosion inhibition is probably due to the adsorption of the Tilia Leafs on the metal surface and blocking its active sites by phenomenon of physical and chemical adsorption.

(4) Tilia Leafs was found to obey Temkin adsorption isotherm from the fit of the experimental data at all the doses studied.

(5) The values of E_a^* obtained in the presence of the Tilia Leafs were lower compared to the blank acid solution which further support the chemical adsorption proposed.

(6) The values of G_{ads}^o obtained are low and negative, which reveals the spontaneity of the adsorption process

(7) The results indicate that, the Tilia Leafs acts as mixed type inhibitor.

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IZVOD

TILIA LEAFS KAO EKOLOŠKI INHIBITOR KOROZIJE ZA MEKI ČELIK U VODENIM RASTVORIMA

Aktivnost ekstrakcije Tilia Leafa kao zelenog inhibitora korozije (ekološki prihvatljiv) za meki elik u 1M HCl testirana je koriš enjem gubitka težine, potentiodinami ke polarizacije i elektrohemijske impedansne spektroskopije (EIS). Dobijeni rezultati pokazuju da je Tilia Leafs ekstrakt odli an inhibitor korozije. Efikasnost inhibicije pove ava se s pove anjem temperature od 25^{0}C do 45^{0}C, dostižu i maksimalnu vrednost od 79% pri najve oj koncentraciji inhibitora od 300 ppm na temperaturi od 45^{0}C. Merenja polarizacije pokazuju da ekstrakt Tilia Leafs deluje kao inhibitor mešovitog tipa. Nikuist-a kriva ilustruje da pri pove anju koncentracije ekstrakta Tilia Leafs prenos naelektrisanja raste i smanjuje se kapacitivnost dvostrukog sloja. Adsorpcija ekstrakta Tilia Leafs na mekom eliku ponaša se po Temkinovoj izotermi adsorpcije.

Klju ne re i: *meki elik, HCl, inhibitori korozije, Tilia Leafs ekstrakt, EIS.*