FICUS CARICA AND OLIVE LEAVES AS ENVIRONMENTAL FRIENDLY CORROSION INHIBITORS FOR ZINC IN HCL SOLUTION.

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Abstract

The inhibiting action of Ficus carica and Olive extracts on the corrosion process of zinc in 2.0 M HCl solution has been investigated by weight loss, open –circuit potential and potentiodynamic polarization measurements. The results revealed that, the highest efficiency (IE%) was observed at 20.0 g/l of inhibitor. Langmuir isotherm was investigated to clarify the nature of adsorption. The values of ΔG^o_{ads} are low revealed to a physical adsorption of the extracts on the zinc surface. The effect of temperature range (25-55°C) supporting the proposed physical adsorption. Electrochemical behaviour indicated that the extract act as anodic- type inhibitors.   .

Key words: zinc, Ficus, Olive, acid medium and inhibitor,polarization

Introduction:

Zinc is one of the most widely used in various industrial operations. The largest use of zinc is as a protective coating for iron, galvanization. The corrosion behaviour of zinc in acid media, via two partial reactions[1]:

i. The partial cathodic reaction involves the evolution of hydrogen gas:

$$2H^+_{(aq)} + 2e \rightarrow H_{2(g)} \tag{1}$$

ii. The partial anodic reaction involves the oxidation of metal and formation of soluble ions:

$$Zn \rightarrow Zn^{++} + 2e \tag{2}$$

Many researchers in the literature studied the corrosion inhibition of zinc in HCl media using organic compounds [2-7]. Recently started to study the natural compounds of some plant extracts as a safe corrosion inhibitors for zinc in acid media [8-12]. There is no reports in the literature on the use of the plant extract of Ficus carica and Olive leaves therefore, the aim of the present work is to examined the effect of Ficus carica and Olive extracts as environmentally friendly corrosion inhibitors for zinc in HCl solution, using chemical and electrochemical measurements.

Experimental:

A cylindrical samples of pure zinc (99.999%) from (Sigma-Aldrich) with apparent area of 3.43 cm^2 were used for weight-loss measurements. For open-circuit

and potentiodynamic polarization studies a cylindrical rod mounted into glass tube by epoxy risen, with an exposed area of 0.50 cm^2. The electrode surface was mechanically polished using successive grads of emery paper down 4/0. Then, degreased with acetone and rinsed with distilled water and dried and immediately weighed. Different concentrations of AR grade of HCl solutions were prepared by an analytical dilution from stock solution.
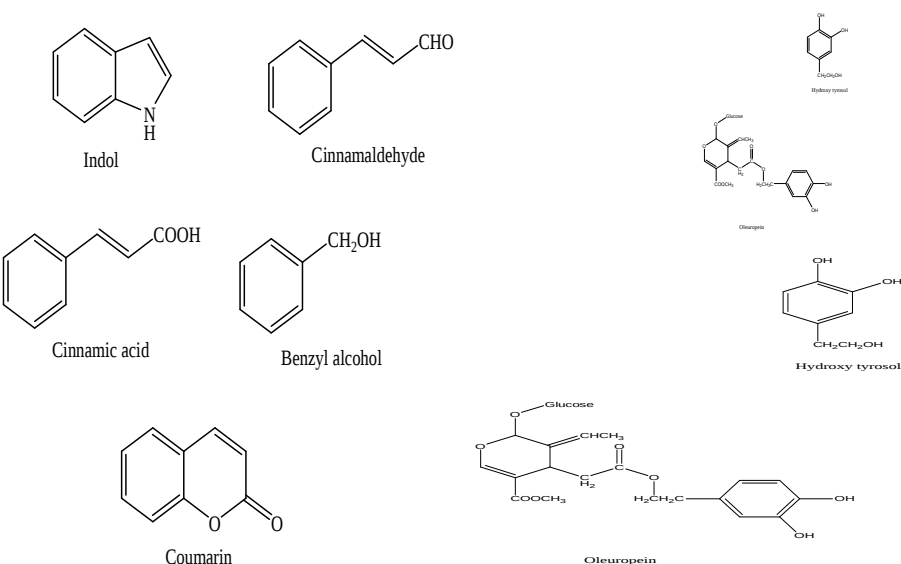
The plants extracts[13,14] as in Figure **(1)**

a

Figure (1): The chemical structure of some compounds in:
a-Ficus carica and b-Olive extracts.

were prepared by boiling weighed amounts of the dried and ground leaves for one hour and left overnight. Then, the solution was filtered and stored. The concentrations of the extracts are expressed as g/l.

The weight loss methods were recorded by the usual procedure[15] at temperature range (25-55°C) with and without different concentrations of the plant extracts. The corrosion rate was determined using the relation:

$$C.R. = \frac{\Delta W}{A \times t \times d} \tag{3}$$

Where ΔW is weight loss, A is the area and t,min is the immersion time, and C.R. was expressed in $g/cm^2.min.$ and d is the density gm/cm^3.

Open-circuit potential measurements were carried out using electronic multimeter (Type GDM-8145). The potentials were recorded with respect to saturated calomel electrode as a reference electrode. The potentiodynamic polarization measurements were performed using three compartment cells with a zinc rod as working electrode, a platinum wire as counter electrode and an Ag/AgCl as reference electrode. Measurements were achieved using Autolab/PGSTAT 30, at scan rate 5 mV/s starting from cathodic potential going to anodic direction. All runs were done at $25^°C$.

Results and discussion:
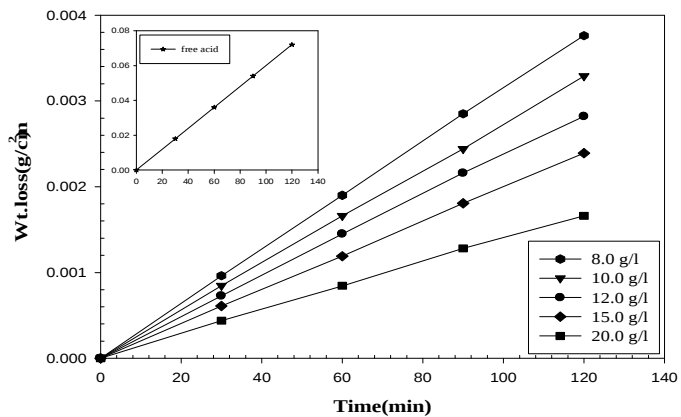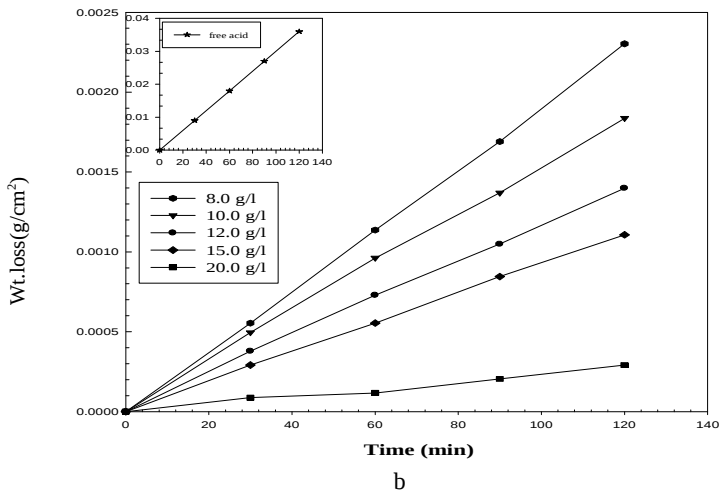
Weight- loss method:

b

Figure (2): **Weight loss-time curves for zinc in 2.0 M HCl solution in absence and presence of different concentrations of :a- Ficus carica and b-Olive leaves extract at 25ᵒC.**

Figure (2) (a,b) represent the weight loss- time curves for zinc sample in 2.0 M HCl as corrosion media at $25°C$ in absence and presence of concentration range (8.0-20.0 g/l) of Ficus carica and Olive extracts. As can be see from the curves the weight loss of zinc in presence of plant extracts varies linearly with time and its lower than obtained in the blank solution. This indicates that the extracts were first adsorbed onto the metal surface and thereafter, inhibits the corrosion process[16]. Also the calculated corrosion rate decreases with increasing the concentration of extracts, indicating that the degree of inhibition depends upon the concentration of inhibitor and the nature of the solution. The inhibition efficiency percent (IE%) of the inhibitors in HCl was acalculated using the following equation[17]

$$IE\% = \left[1 - \left(\frac{C.R._{inh}}{C.R._{free}} \right) \right] \times 100$$

(4) Where $C.R._{free}$ and $C.R._{inh}$ are the corrosion rates in free and inhibited solutions, respectively. The variation of the concentration and IE% for Ficus carica and Olive leaves extracts in 2.0 M HCl are shown in Figure(3).
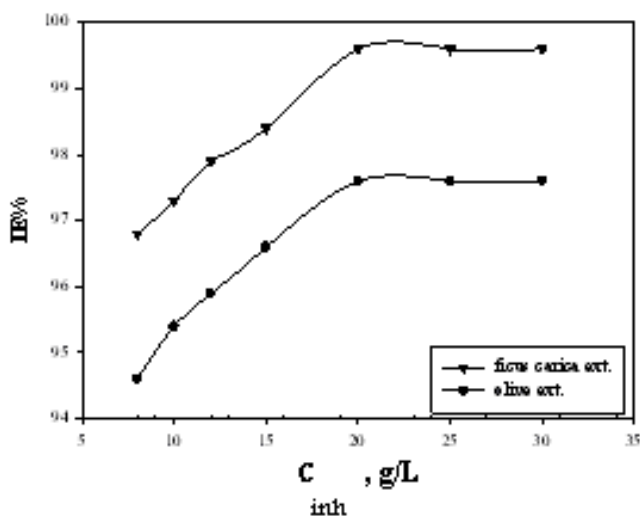

Figure (3):Variation of inhibition efficiency with concentration of Ficus carica and
**   Olive leaves extracts for zinc in 2.0 M HCl solution at**
$25°C$.

   The curves are(S-shape) and characterized by initial rising of IE % with concentration indicating a formation of monolayer

adsorbate film on zinc surface, until reached to steady state at 20.0 g/l. The increase of extracts concentration above this value the inhibition efficiency remained more or less constant suggesting a complete surface coverage by the extracts molecules. The degree of the surface coverage θ which represents the part of the metal surface covered by inhibitor molecules was calculated using the following equation[18].

$$\theta = 1 - \left(\frac{C.R_{inh}}{C.R_{free}} \right)$$

(5)

Where $C.R._{free}$ and $C.R_{inh}$ are the corrosion rates of zinc in HCl in absence and presence of different concentrations of inhibitors.

The values of $C.R$, IE% and θ for different concentrations of Ficus carica and Olive leaves extracts in HCl are listed in Table (**1**). Inspection of this Table, the data revealed that as the plant extract concentration increases, the corrosion rate decreases, while the inhibition efficiency percent IE%, and surface coverage θ , increase. This behaviour may be attributed to increase in the surface coverage θ due to increase of the number of adsorbed molecules on zinc surface. A good efficiency is observed at constant concentration of plant extracts (20.0 g/l), with IE% of Ficus carica and Olive leaves extracts in HCl are 99.67% and 97.67%, respectively. It can be concluded that the Ficus carica and Olive leaves extracts act as an excellent inhibitors for corrosion of zinc in HCl solution.

Table (1): Effect of extract concentrations on ($C.R$), ($IE\%$) and (θ) for zinc in 2.0 M HCl solution at 25ºC.

Conc. (g/l)	Ficus carica leaves extract			Olive leaves extract		
	C. R (g/cm².min)	IE%	θ	C. R (g/cm².min)	IE%	θ
0.00	6.01×10^{-4}	0.00	0.00	6.01×10^{-4}	0.00	0.00
8.0	1.89×10^{-5}	96.85	0.9685	3.20×10^{-5}	94.66	0.9466
10.0	1.60×10^{-5}	97.33	0.9733	2.76×10^{-5}	95.40	0.9540
12.0	1.21×10^{-5}	97.99	0.9799	2.42×10^{-5}	95.97	0.9597
15.0	9.21×10^{-6}	98.46	0.9846	1.98×10^{-5}	96.68	0.9668
20.0	1.94×10^{-6}	99.67	0.9967	1.40×10^{-5}	97.67	0.9767

The interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm. For the extracts under test it was found that the Langmuir adsorption isotherm[19] fits the experimental data, of given by:

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

(6)

Where K is binding constant of adsorption reaction and can be calculated from the reciprocal of the intercept. The relation between C/θ and C at 25°C in 2.0 M of HCl solution with various concentrations of Ficus carica and Olive leaves extracts is shown in Figure (**4**).
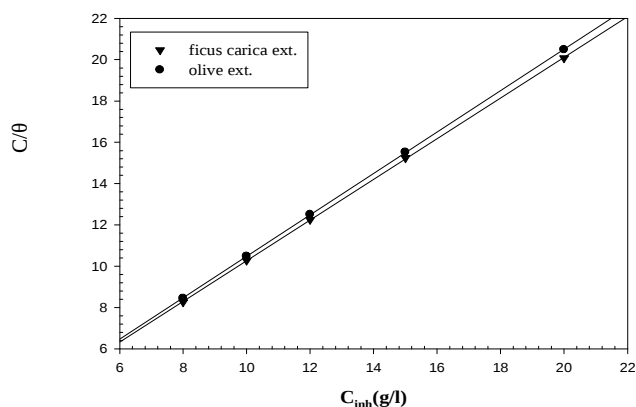

Figure (4): Langmuir adsorption plots for zinc in 2.0 M HCl with different concentrations of plant extracts at 25ºC.

Inspection of this Figure reveals that a straight line was obtained with slops close to unity indicating that the adsorption of plant extracts obey Langmuir adsorption isotherm. These involves the assumption of no interaction between the adsorbed inhibitor constituents on the zinc surface[20]. The relation between binding constant, K and the standard free energy change of adsorption ΔG^{o}_{ads} is given by the following equation[19]:

$$K = \left[\frac{1}{55.5}\right] \exp \left[\frac{- \Delta G^{o}_{ads}}{RT}\right]$$

(7)

Where 55.5 is the molar concentration of water in solution, R is the gas constant (8.314 J/mol/degree) and T is the absolute temperature.

The calculated values of standard free energy change ΔG^{o}_{ads} and binding constant K, for the plant extracts in 2.0 M HCl are shown in Table (**2**). The values of K are relatively small indicating that the interaction between the adsorbed extracted molecules and zinc metal surface is physically adsorbed. Generally, values of ΔG^{o}_{ads} until -20 KJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physical adsorption)[21]. The values obtained of ΔG^{o}_{ads} suggests a physical adsorption of Ficus carica and Olive leaves extracts on the zinc surface in HCl solution and the negative sign indicates that the adsorption of extract molecules on the zinc surface is a spontaneous process.

Table (2): Binding constant (K) and standard free energy change of adsorption ΔG^{o}_{ads}
for plant extracts in 2.0 M HCl at 25ºC.

Plant extracts	K (g^{-1} l)	$-\Delta G^{o}_{ads}$ KJ mol^{-1}
Ficus carica	2.3479	12.07
Olive leaves	2.1570	11.86

The effect of temperature range (25-55ºC) on the corrosion behaviour and the inhibition efficiency of zinc in HCl solution in presence of 15.0 g/l of Ficus carica and Olive leaves extracts, was studied by weight loss method. The data in Table (**3**) indicate that

the corrosion rate of zinc in absence and presence of the plant extracts increased with increasing in temperature. This is due to that the increase in temperature usually accelerates corrosion processes, particularly in acid media in which H_2 gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal[1]. The values of $IE\%$ of the extracts decrease with increasing temperature, and the high inhibition efficiency at 25°C. This result suggests a physical adsorption of Ficus carica and Olive leaves extracts on the corroding zinc surface. The physical adsorption mechanism, obtained from electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal due to the electric field existing at the metal / solution interface. A negative surface charge will favour the adsorption of cations whereas, anion adsorption is favoured by positive surface charge. A corroding zinc specimen under test carries a negative surface charge in hydrochloric acid solution, since the Ficus carica and Olive extracts are a polar molecules, physisorpotion could occur with the negatively zinc surface. On the other hand, the ability of Cl^- ions in hydrochloric acid solution to pick up the cations appear in the solution and facilitate the physical adsorption of inhibitor cations on the negatively charged surface by electrostatic interaction.

Table (3): Effect of temperature on the corrosion rate ($C.R$) and efficiency ($IE\%$) for zinc in 2.0 M HCl in absence and presence of plant extracts.

Temp. (°C)	2.0 M HCl	Ficus carica extract		Olive leaves extract	
	$C.R$ (g/cm^2.min)	R_{corr} (g/cm^2.min)	IE%	$C.R$ (g/cm^2.min)	IE%
25	6.01×10^{-4}	9.23×10^{-6}	98.46	1.99×10^{-5}	96.68
35	6.45×10^{-4}	2.23×10^{-5}	96.54	2.92×10^{-5}	95.47
45	7.56×10^{-4}	3.25×10^{-5}	95.75	4.81×10^{-5}	93.63
55	1.01×10^{-3}	5.58×10^{-5}	94.47	7.48×10^{-5}	92.59

The apparent activation energies (E_a^*) for the corrosion process in absence and presence of plant extracts were evaluated from Arrhenius equation[22]:

$$\log C.R = \log A - \left[\frac{E_a^*}{2.303RT}\right]$$

(8)

Where $C.R$ is the corrosion rate (g/cm^2.min) , A is the constant frequency factor and E_a^* is the apparent activation energy, R is the gas constant (8.314 J/mol/degree) and T is the absolute temperature. By plotting of logarithm of C.R of zinc in HCl acid in absence and presence of 15.0 g/l of extracts, versus the reciprocal of absolute temperature range (25-55°C), give straight lines with slope equal to $- E_a^* / 2.303R$ as represented in Figure (**5**).
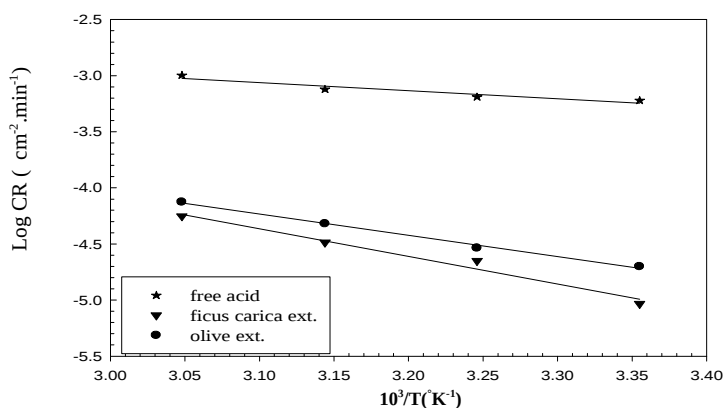

Figure (5): Arrhenius plots of the corrosion rate for zinc in 2.0 M HCl solution in absence and presence of plant extracts.

The activation thermodynamic parameters of zinc corrosion in HCl medium in absence and presence of extracts under test are given by Eyring equation[22]:

$$C.R = \left[\left(\frac{RT}{Nh}\right)\right] \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right)$$

(9)

Where h is Plank's constant, N is Avogadro's number, ΔS^* and ΔH^* are the activation entropy and enthalpy changes, respectively. A plot of $\log C.R/T$ versus $\dfrac{1}{T}$ gives straight line with slope of $[(-\Delta H^*/R$] and an intercept of $\left[\log(R/Nh) + \left(\Delta S^*/2.303R\right)\right]$, represented in Figure (**6**).
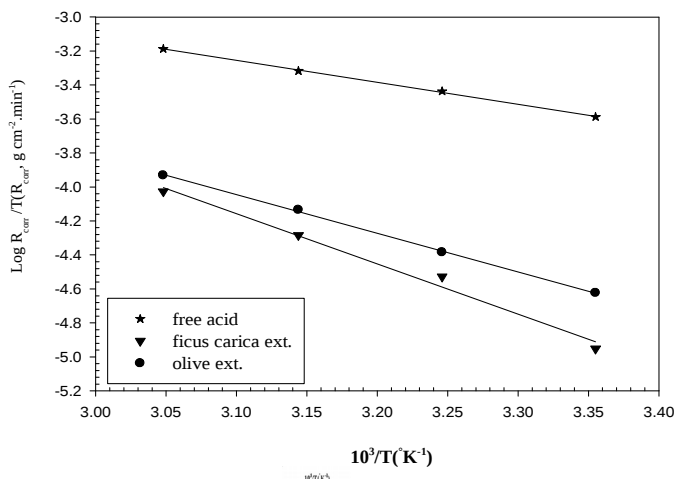
Figure (6): Eyring plots of the corrosion rate for zinc in 2.0 M HCl solution in   absence and presence of plant extracts.

The values of activation parameters are listed in Table (**4**). It is clear that, the presence of Ficus carica and Olive extracts in HCl acid increase the values of E_a^* comparing to its uninhibited, these attributed to an appreciable decrease in the adsorption process of the inhibitors on the metal surface with increasing temperature and a corresponding increase in the reaction rate because of the greater area of the metal that is exposed to the acid solution and corrosion inhibition occurred through physical adsorption[23]. The higher ΔH^* values in presence of the extracts indicate that the degree of surface coverage decreased with rise in temperature, supporting the proposed physisorption mechanism. Also the values of ΔS^* in the absence and presence the extracts is negative meaning that the increasing in ordering accompanied the dissolution process.

**Table (4): Activation parameters of zinc** in 2.0 M HCl in absence and presence of plant extracts.

Plant extract	E_a^* $KJ\,mol^{-1}$	ΔH^* $KJ\,mol^{-1}$	ΔS^* - $J\,mol^{-1}\,{}^oK^{-1}$
Free acid	13.677	16.33	157.57
Ficus carica	47.10	49.68	79.09
Olive leaves	36.08	38.90	110.02

Open-circuit potential measurements:

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Figure (**6**) represent the variation of potential of zinc electrode with time in aerated solution of 2.0 M HCl in absence and presence of different concentrations of Ficus carica and Olive leaves extracts. Inspection of the curves of the free acid the behaviour can be classified into two parts, the first one exhibit a general tendency for open-circuit potential to shift from less negative to more negative values (corrosion process), this may be attributed to the destruction of pre-immersion oxide film present on the surface of zinc electrode in acid medium. The second part of the curves, the potential shifts gradually from the more negative towards to the positive direction and thereafter it remains almost constant for a long time. According to Evan's[24], the shift of electrode potential towards nobler values signify the repair and further thickening of the air-formed pre-immersion oxide film on the surface of the metal. In the presence of the extracts, the open-circuit potential drift with time towards a positive potential and the time for which the steady state values were reached depends upon the nature of extract. Also it shows that Ficus carica and Olive extracts in high concentration (20.0 g/l), were effective in retarding or preventing the corrosion process because this additive shifts the potential towards more noble values. This may be due to the adsorption of the inhibitors on an oxide-free metal surface and prevention the hydrogen evolution reaction at the cathodic sites. The inhibition increases the protection qualities of the oxide surface or other surface layer from the aggressive solutions. The fundamental step involves displacement of pre-adsorbed water molecules by the extract inhibitors followed by electrostatic force reaction at the surface[23].
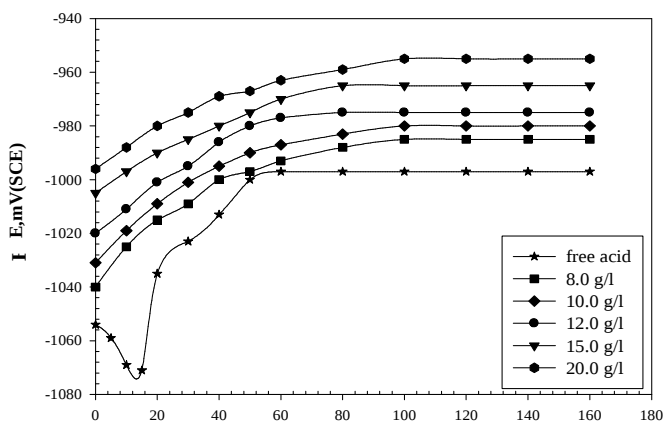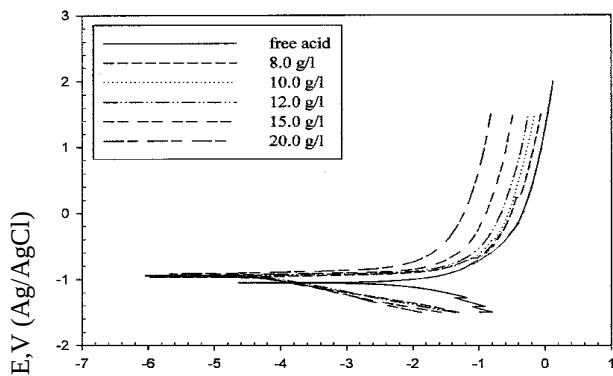
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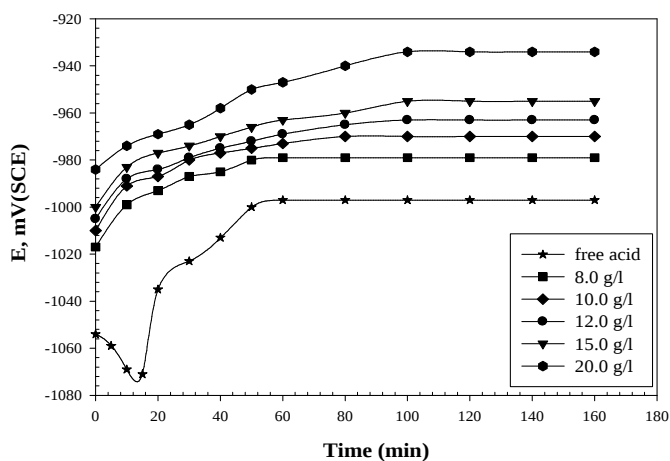
b

Figure (7): The variation of the open-circuit potential for zinc electrode in 2.0 M HCl with different concentrations of : a-Ficus carica and b-Olive extract at 25°C.

Potentiodynamic polarization measurements:

A typical potentiodynamic polarization curves for the zinc electrode in aerated 2.0 M HCl solution in absence and presence of different concentrations
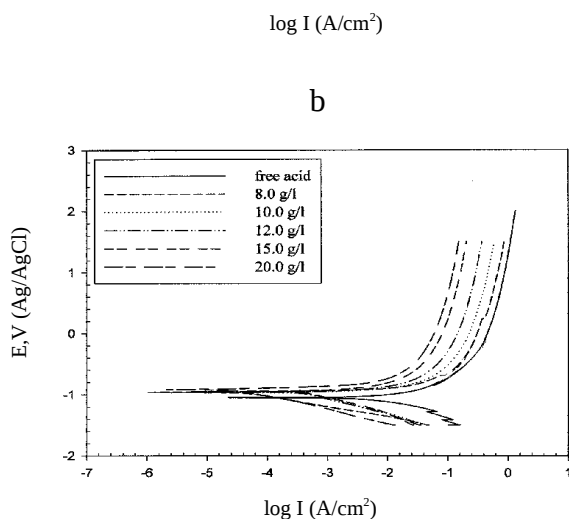
a

log I (A/cm^2)

b

Figure (8): Potentiodynamic polarization curves for zinc electrode in 2.0M HCl in absence and presence of different concentrations of A-Ficus carica and B- Olive extract at 25°C.

The shape of the curves are not modified on adding the plant extracts or by increasing the concentration, but the more pronounced behaviour that the curves produces a little shift on the cathodic region and a great shift on anodic region. The adsorbed inhibitor[23] blocks either the anodic or cathodic reaction or both. The effect of the inhibitor may be due to the charges in the electric double layer, by reducing the metal reactivity, or by the inhibitor participation in partial electrode reaction and by formation of physical barrier. The adsorbed inhibitor may not cover the entire metal surface, but occupies sites which are electrochemically

active and thereby reduced the extent of anodic or cathodic reactions or both. The corrosion rate will be decreased in proportion to the extent to which the electrochemically active sites are blocked by the adsorbed inhibitor, this is represented by the Figure **(9)**.
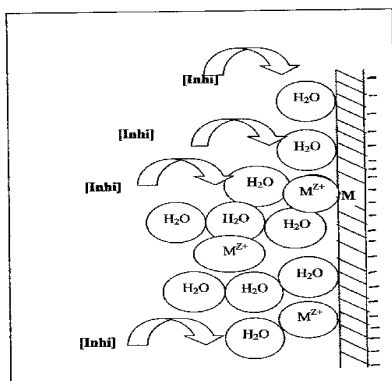

Figure (9): Adsorption of the inhibitor by physical blocking

The electrochemical parameters E_{corr}, I_{corr}, b_c, b_a and IE% are given by equation:

$$IE\% = \left[1 - \frac{(I_{corr})_{inh}}{(I_{corr})_{free}}\right] \times 100$$

(10)

Where $(I_{corr})_{free}$ and $(I_{corr})_{inh}$ refer to the corrosion current densities in absence and presence of inhibitor respectively and can be determined by extrapolation of cathodic and anodic Tafel lines to corrosion potential. Electrochemical parameters are collected in Table (**5**). Inspection of this Table, it is observed that the corrosion potentials E_{corr} shifts to less negative values (noble direction) with increasing the extracts concentration. This indicates that the addition of Ficus carica and Olive leaves extracts primarily affect the anodic process, and acts predominately as anodic-type inhibitors. Consequently, the adsorption of the extracts in HCl solution are more likely at anodic sites. Also, the values of the corrosion current density (I_{corr}) decreased with increasing the concentration of the extracts, indicating that the inhibitive property of these extracts on the corrosion of zinc in acid solution. Tafel

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slopes, b_c and b_a are more or less constant upon increasing the extract concentrations. These results indicate that the extracts act by simple blocking the available cathodic and anodic sites on zinc surface. In the other word, these inhibitors decreases the surface area for corrosion without affecting the mechanism of corrosion process and only cause inactivation of a part of the metal surface with respect to corrosive medium. Also the inhibition efficiency, $IE\%$ for extracts in 2.0 M HCl solution increases with increasing concentration, and at certain concentration (20.0 g/l), $IE\%$ reaches 98.79%, 93.91% for Ficus carica and Olive leaves extracts, respectively. The results of the electrochemical measurements are in a good agreement with the chemical method.

Table (5): Electrochemical parameters and inhibition efficiency for zinc electrode in 2.0 M HCl in absence and presence of different concentrations of Ficus carica extract at 25ºC .

Conc. (g/l)	$-E_{corr}$ (V)	I_{corr})A/cm^2)	$-b_c$ (V/dec)	b_a (V/dec)	Rp (Ω.cm^2)	IE%	R_{corr} (mpy)
0.00	1.06	3.977×10^{-3}	0.107	0.10	2.309	0.00	4.677×10^{-4}
8.0	0.961	9.025×10^{-5}	0.187	0.021	30.827	97.73	1.061×10^{-4}
10.0	0.954	7.477×10^{-5}	0.165	0.023	40.257	98.11	8.793×10^{-5}
12.0	0.941	6.625×10^{-5}	0.205	0.023	40.287	98.33	7.791×10^{-5}
15.0	0.935	6.107×10^{-5}	0.162	0.019	60.07	98.46	7.182×10^{-5}
20.0	0.913	4.798×10^{-5}	0.199	0.031	100.106	98.79	5.642×10^{-5}

Inhibition mechanism of plant extracts:

Ficus carica under test contains mixture of benzyl alcohol and aromatic compounds (Cinnamic aldehyde, Cinnamic alcohol) and a nitrogen containing compound (indol). The aqueous extracts of Olive contains polyphenolic compounds, the major constituents are oleuropein ($C_{25}H_{32}O_{13}$) and hydroxytyrosol (3,4-dihydroxphenylethanol). Oleuropein is readily hydrolyzed into elenolic and hydroxytyrosol[14] , these latter may be play the major role in the inhibition process. The presence of oxygen atoms in both extracts as in phenolic, aldehyde and alcoholic may be responsible for adsorption on zinc surface through the lone pair of electrons present on the oxygen atoms which decrease the electronic density at an adsorption centers of plant extracts

molecules on a negative charged zinc surface, the physical adsorption determined by electrostatic attraction and forming a covering film. The aromatic cycles repel the aqueous solution out of the electrode surface leading to inhibition of the attack of the aggressive solution on the metal. Therefore, it could be concluded that the Ficus carica and Olive leaves extracts act as an excellent corrosion inhibitors for zinc in aerated solution of HCl by using chemical and electrochemical techniques.

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Conclusions:

1- The corrosion process is inhibited by adsorption of the extracts on zinc surface follows Langmuir isotherm, in which one molecule of inhibitor occupying one active site.
2- The inhibition efficiency of the extracts under test decreases with the rise in temperature and the apparent activation energy increases in presence of inhibitors.
3- Open-circuit and polarization measurements indicate that the plant extracts in HCl medium act as anodic- type inhibitors.
4- The inhibition efficiency obtained from polarization measurements show a good agreement with those obtained from comparative weight loss determinations.

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