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The use of *Ruta chalepensi* as corrosion inhibitor for steel corrosion in 2M sulphuric acid solution

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ABSTRACT

The effect of addition of *Ruta Chalepensi (**RC**)* extracts (aqueous extract and alcoholic extract) on steel corrosion in 2.0 M H_2SO_4 containing 10% ethyle alcohol (EtOH) by chemical methods (hydrogen evolution (HE) and mass loss(ML)) and electrochemical (potentiodynamic polarization (PDP) and impedance (EIS)) methods. SEM was applied for surface morphology to confirm the obtained results. The results showed that when the concentration of the extracts is increased the corrosion rate of steel sample is decreased, which indicates that the inhibition of the corrosion takes place. The polarization results showed that the extracts of *RC plant* acts as mixed type inhibitors, they retarded both cathodic and anodic corrosion reactions. The electrochemical parameters ($E_{corr.}$, $I_{corr.}$, b_c and b_a) and the inhibition percentages inh. were calculated. Electrochemical impedance spectroscopy results showed that the corrosion and corrosion inhibition of steel occurred mainly by charge transfer. Also, the experimental results from chemical and electrochemical results agree with Langmuir isotherm. Values of equilibrium constant of adsorption Kads. and the standard free energy of adsorption $\Delta G°_{ads.}$, for the extracts were also calculated.

Key words: Steel, acid solution, corrosion, inhibition and *Ruta chalepensi*.

INTRODUCTION

The study of metals corrosion in acidic solutions of important studies for industry, where utilized in chemical cleaning acid is also used in many industrial fields such as washing acid, remove the crust, process wells oil in addition to many different industrial processes[1]. Because of the high ability of acids to dissolve minerals, so it is required to find a way to reduce waste, the amount of metals chemically treated and thus reduce economic losses and health, various means of protection have been proposed to protect metals from corrosion, it has made numerous efforts and successful use of preventive strategies to reduce the corrosion including the use of organic and inorganic compounds as corrosion inhibitors, where the addition of inhibitors is one important practical way and effective to protect the metals against the corrosion, especially in acidic media because of their highly controlled process of dissolving metal[2].

Metal use of countries increases with technologic and economic development. However, destruction of metals by environmental factors is the main problem for the industrial companies. Metal and alloys that come into contact with acids are susceptible to corrosion because of their thermodynamic instability in the acid system[3]. Many metals and alloys used in the industries and human activities of the types of corrosion different view of the presence among corrosive, the metals such as steel, aluminum, zinc and nickel, where one of the important minerals used in various industrial applications such as shipbuilding, pipelines water, batteries, mechanical, chemical and others[4-9].

The iron, steel and their alloys are the most common metals for uses, so they are exposed to the process of corrosion as a result of exposure to different corrosive media is that exposure to wet air. Therefore, the choice of metal is usually not on the basis of its characteristic properties in terms of power and ease of manufacturing and the price but also on the basis of its resistance to corrosion in the used medium. In general, all types of steel and metal alloys corroded at a remarkable rate in moist conditions where corrosion rate increases significantly as a result of the presence of pollution and humidity in the atmosphere[10].

The common way for corrosion protection is to use durable material. But this way is impossible owing to economic causes in the complex and wide process such as, the acid system. The most common way is use the inhibitor to reduce corrosion in this condition[3].

Inhibitors are substances which are added in small quantities to the humid (wet) corrosion environment works to protect the metal from corrosion processes to reduce corrosion by inhibiting the cathodic processes and / or the anodic processes. Therefore, the importance of using inhibitors continues to grow to control and reduce the corrosion of metals[11].

In general, the natural products have a promising future for the use of retardants to corrosion in addition to their use of medical treatment for several diseases were selected for the following reasons:

- Contain organic compounds containing a single pairs of electrons and / or multiple double bonds, or both[12].
- Is an alternative to toxic chemicals and are commonly used in industry as 3 disincentives to the process of corrosion.
- The tropism to the plant extracts gives major benefits; seeing the accessibility of the remains of plants and cheap canned food industry.
- It contains the new effective compounds in inhibiting corrosion and is environmentally safe.

However, the problem of finding an inhibitor that has little or no impact on the environment has attracted numerous researches in recent times[13]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds[14]. Most green corrosion inhibitors are obtained from ethanol, aqueous, acid, methanol, or formaldehyde extract of plant materials[15]. The uccessful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environments has been reported by some research groups[16-23].

The present study is aimed to investigating the adsorption and inhibitive properties of aqueous extract and alcoholic extract of leaves of *Ruta Chalepensi (RC)* plant for the corrosion of steel in H_2SO_4 solutions.

Definition of *Ruta Chalepensi (RC)*, Fig. (1)

Scientifically known as Ruta graveolens. There are in the Kingdom is scientifically known as Ruta chalepensis L, and this plant is characterized by a large number of chemical compounds such as coumarins and furocoumarins alkaloids and alkaloids derived from bio-synthesis Anthranilic acid. It is also contains quinolines, furoquinolines and acridons. And is characterized by the presence of triterpenes such as Limonoid, Table 1 [24,25].

In a medical point the twigs and new growth buds of the *RC* plant are used against headache, convulsion and when used externally to be irritating to the skin so they are useful for the treatment of vitiligo, herpes, and muscle stiffness, pain and articular inflammation. The oil extracted from the *RC* plant used as anthelmintic and anticolic and menstrual diuretic, however, it caution to use during pregnancy because it causes abortion.

EXPERIMENTAL

Materials preparation

The metal used for the study was steel electrode of the chemical composition was (wt %) Mn (0.5), P (0.035), C (0.38), Si (0.4), S (0.03), Cr (0.9) and Fe (97.61). The steel electrode was bolished first with emery paper of type (231Qwetordry Imperial Papel Aesco), the spectrum of starting paper more roughness to the more softer, then the sample wash with bidestilled water and ethyl alcohol (AR) and then dried with stream of cold air, so the sample is ready immersed in a solution of the test after the Ht appointment of its dimensions.

All solutions used are the degree of high purity, sulfuric acid (H_2SO_4) was used (PAIPanreac) with concentration of 2.0 M H_2SO_4 containing 10% EtOH (PAI-Panreac) as a major test solution.

Preparation of inhibitor

Two types of extracts of *Ruta Chalepensi (RC)* plant have been prepared as follows:

Alcoholic extract:

The dry and ground 350g. of *RC* plant was extracted with methyl alcohol (MeOH) for a period of seven consecutive days by adding a sufficient amount of MeOH (100ml-700ml) to the ground plant and leave to the next day and then filtrate and taken the filtrates were further subjected to evaporation and then add methyl alcohol to the plant again and repeat the same steps the next day to the conclusion that the color becomes light green, the filtrate is collected from each extract and left to evaporate and is then dissolved in ethyl alcohol and placed in a standard flask 250ml.

Aqueous extract

Weighed 200g. of *RC* plant and extracted with warm bidestilled water of about 500ml. and filtered several times and then taken filtrate of all time, is to repeat the same steps as in the extraction with alcohol and placed in a standard flask capacity 250ml. Methods of measurement

Three methods of measurements were used in this study there are:

- Chemical Technique
- Electrochemical Technique
- Scanning Electron Microscopy

The chemical technique

This method is done in two ways, hydrogen evolution method (HEM) and mass loss method (MLM).

Hydrogen Evolution Measurements

Hydrogen evolution measurements were carried out at 30p C as described in literature [26]. From the volume of hydrogen gas evolved per minute, inhibition efficiency (%I), degree of surface coverage (Θ) and corrosion rate (R) were calculated using equations 1, 2 and 3, respectively:

$$\%Inh._{HE} = 1 - V^{1}_{Ht} / V^{o}_{Ht} \times 100 \quad ...(1)$$

$$\Theta = \%I/100 \quad ...(2)$$

$$R\ (ml\ min^{-1}cm^{2}) = (V^{o}_{Ht} - V^{1}_{Ht}) / t \quad ...(3)$$

where V^1_{Ht} is the volume of hydrogen gas at time t for inhibited solution and V^o_{Ht} is the volume of hydrogen gas evolved at time t for uninhibited solution.

Mass Loss Measurements

After complete of each test steel sample is separated from the test solution, washed with bidistilled water and with ethyl alcohol, dried with a stream of cold air and then re-weighing. From the weight loss results, the inhibition efficiency (%I) of the inhibitor, degree of surface coverage and corrosion rates were calculated using equations 4, 5 and 6, respectively:

$$\%Inh._{ML} = (1 - W_1/W_2) \times 100 \quad ...(4)$$

$$\Theta = 1 - W_1/W_2 \quad ...(5)$$

$$R'\ (g\ min^{-1}cm^{-2}) = W/At \quad ...(6)$$

where W1 and W2 are the weight losses (g/dm^3) for steel in the absence and presence of inhibitor in H_2SO_4 solution, respectively, Θ is the degree of surface coverage of the inhibitor, A is the area of the steel electrode (in cm^2), t is the time of immersion (in minutes) and W is the weight loss of steel after time t.

Electrochemical technique

Two types of electrochemical measurements has been applied which are potentiodyanamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) measurements, this measurements was obtained by using impedance spectrum analyzer of the kind ACM instrument, Auto Tafel and ACDSP)), relating to a computer. (Bridge DVD ASUS 8X max). From electrochemical measurements (PDP and EIS), the inhibition efficiency is calculated from equations 7 and 8 as follows:

$$\%\mathrm{Inh.}_{\mathrm{P}} = (1 - \mathrm{I}_{\mathrm{corr.}}/\mathrm{I}^{\circ}_{\mathrm{corr.}}) \times 100 \quad ...(7)$$

$$\%\mathrm{Inh.}_{\mathrm{Rct}} = (1 - \mathrm{R}^{-1}_{\mathrm{ct}}/\ \mathrm{R}^{-1}_{\mathrm{cto}}) \times 100 \quad ...(8)$$

where $I_{corr.}$ and $I°_{corr.}$ are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential, R^{-1}_{ct} and R^{-1}_{cto} are the charge transfer resistance values with and without inhibitor, respectively.

Scanning Electron Microscopy (SEM) Analysis

The sample under study was imaged using the Scanning Electron Microscope XL 20 PHILIPS insterument to study the effect of the components on the electrode surface at different concentrations of the extracts under study, where the flaming of the samples by SEM technique was doing as follows:

- Sample clean and dry before placing them in any solution.
- The clean sample immersed in 2.0 M H_2SO_4 solution containing 10% EtOH for 60minutes.
- The clean sample immersed in an acid solution containing different concentrations of inhibitors under study for 60 minutes after washing with bidistilled water and then dried and preparing for electron microscopy.

RESULTS AND DISCUSSION

Chemical Study

Figure (2) shows the relation between hydrogen evolution with time for the corrosion of steel in 2.0 M H_2SO_4 solution containing 10% EtOH in absence and presence of different concentrations of aqueous extract and alcoholic extract of *Ruta chalepensis (RC)* at 30°C. It is clear that the evolution of hydrogen gas begins after a certain time called induction period which corresponds to the time needed to break the oxide layer formed on the surface of steel after immersing the sample directly in the corrosive solution, and then the evolution of hydrogen gas varies linearly with time. It is noted that increasing the concentration of an aqueous extract and/or alcoholic extract of *RC* plant the rate of hydrogen gas evolution decreases and the induction period disappear, this means that the decrease the corrosion rate of the steel sample under study, which indicates an inactivation process, results also indicate that the presence of aqueous extract and/or alcoholic extract of *RC* plant detract the slope of the straight line substantially. This corresponds to the corrosion rate of steel sample, i.e., these extracts impede the corrosion of steel in the studied solutions. The corrosion rates (R and R') and inhibition efficiencies (%Inh.HE and %Inh.ML) for steel sample were calculated in absence and presence of different concentrations of aqueous extract and / or alcoholic extract of *RC* plant at 30°C from hydrogen evolution(HE) and mass loss(ML) measurements, respectively and recorded in the Tables (2 and 3).

It is clear from the Tables that the corrosion rate of steel decrease with increasing concentration of *RC* plant extracts under study and both aqueous and alcoholic extracts of *RC* plant have good ability to reduce the corrosion rate of steel in acid solution, as evidence from the tables that by increasing the concentration of extracts studied more effective inhibition, which proves the effectiveness of the *RC* plant in the inhibition of steel corrosion in H2SO4 acid and the process of inhibition depends on the kind of the extract, and it is noted that the alcoholic extract of *RC* plant has a capacity to inhibit the corrosion of steel greater than those of aqueous extracts.

Inhibition efficiencies (%Inh.) were calculated from HE (%Inh.HE) and ML (%Inh.ML) measurements of equations (1 and 4).

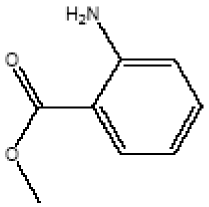
The relationship between logR and / or logR ' versus log C is plotted (Figures (3 and 4)). It is found that they gave a straight lines for both extracts under study. From the straight lines, it observed that the corrosion of steel in 2.0 M H_2SO_4 followed first order reactions.

Electrochemical Study

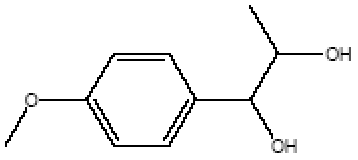
Potentiodyanamic polarization measurements (PDP)

Figure (5) shows the polarization curves

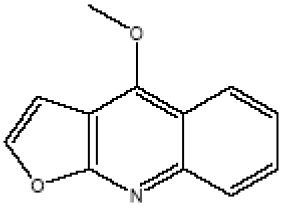
Table 1: Main constituents of *Ruta Chalepensis(RC)*



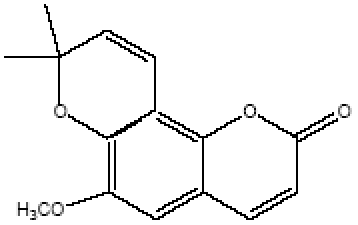
Methyl anthranilate



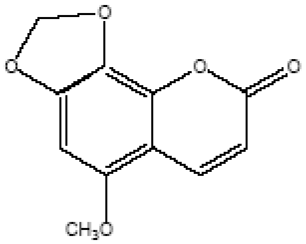
anethole glycol



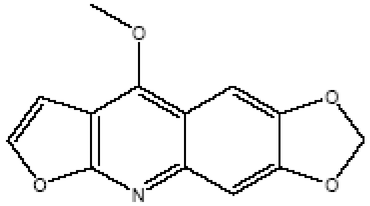
4-methoxyfuro[2,3-b]quinoline



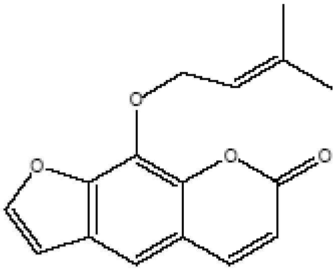
Braylin



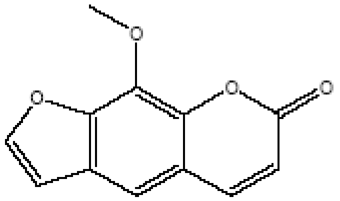
Sabandinin



Maculine



Imperatorin



xanthotoxin

Table 2: The corrosion rates and inhibition efficiencies of steel sample in 2.0 M H_2SO_4 +10%EtOH in absence and presence of different concentrations of *RC* aqueous extract at 30°C.

C(w/v)	**0.0**	**4.0×10^{-3}**	**8.0×10^{-3}**	**11.2×10^{-3}**	**1.4×10^{-2}**	**1.96×10^{-2}**	**8.0×10^{-2}**	**1.6×10^{-1}**
R	6.660×10^{-2}	4.780×10^{-2}	3.749×10^{-2}	3.359×10^{-2}	2.075×10^{-2}	7.793×10^{-3}	5.289×10^{-3}	0.0
R.	9.709×10^{-5}	7.587×10^{-5}	5.677×10^{-5}	5.318×10^{-5}	3.357×10^{-5}	1.626×10^{-5}	9.417×10^{-6}	3.557×10^{-6}
%Inh.HE	-	28.18	43.67	49.53	68.82	88.30	92.05	100
%Inh.ML	-	21.86	41.52	45.22	65.42	83.26	90.30	96.35

Table 3: The corrosion rates and inhibition efficiencies of steel sample in 2.0 M H_2SO_4 +10%EtOH in absence and presence of different concentrations of *RC* aqueous extract at 30°C.

C(w/v)	**0.0**	**4.0×10^{-3}**	**8.0×10^{-3}**	**11.2×10^{-3}**	**1.4×10^{-2}**	**1.96×10^{-2}**	**8.0×10^{-2}**	**1.6×10^{-1}**
R	6.660×10^{-2}	5.500×10^{-2}	3.600×10^{-2}	2.310×10^{-2}	8.08×10^{-3}	0.0	0.0	0.0
R’	9.709×10^{-5}	8.209×10^{-5}	5.267×10^{-5}	3.590×10^{-5}	1.600×10^{-5}	8.573x10-6	8.064×10^{-7}	1.351×10^{-6}
%Inh.HE	**-**	17.72	45.95	65.47	87.00	100	100	100
%Inh.ML	**-**	15.45	45.75	63.03	83.52	91.17	99.17	99.86

of steel corrosion in 2.0 M H_2SO_4 containing 10% EtOH in absence and presence of different concentrations of aqueous extract and alcoholic extract of *RC* plant at 30°C, where the electrochemical parameters and the inhibition percentages (%Inh.P) were recorded in Tables (4 and 5). It is found from polarization study that the aqueous extract and alcoholic extract of *RC* plant hinder both anodic reaction (metal dissolution) and cathodic reaction (hydrogen gas evolution) this shown by displacement the Tafel lines in both anodic and cathodic directions, this means that the aqueous and alcoholic extracts of *RC* plant react as mixed type inhibitors. Also, it clear that increase the concentration of each of the aqueous extract and alcoholic extract of the *RC* plant leads to a gradual decrease in the values of current density (Icorr.) for the corrosion rate of steel sample under study.

Fig. 1: *Ruta chalepensi* (RC) plant

Fig. (6) shows the relationship between the corrosion current (Icorr.) with the logarithm of concentration of the extract (logC). The increase in concentration of both aqueous extract and alcoholic extract of *RC* plant lead to a decrease in Icorr. values

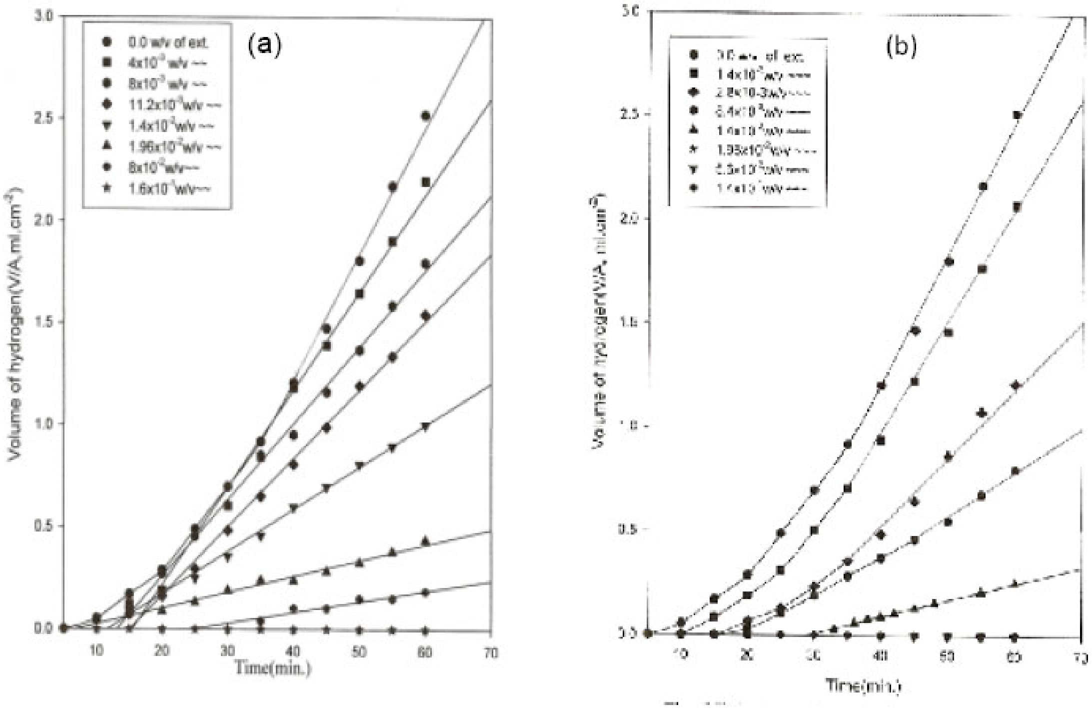


Fig. 2: Volume of hydrogen / time curves of steel corrosion in 2.0 M H_2SO_4 +10% EtOH in absence and presence of different concentrations of *RC* plant a) aqueous extract and b) alcoholic extract at 30°C

which indicates the ability of aqueous extract and alcoholic extract of *RC* plant to inhibit the corrosion of steel under study in H_2SO_4 acid solution. Inspection the Tables (4 and 5) reflect the following:

- The presence of irregular displacement in Ecorr. values to completely lower (more positive) values for steel sample in the presence of aqueous extract and / or alcoholic extract of *RC* plant for the reference solution (blank) (the irregular displacement was appear in the alcoholic extract more than that in the aqueous extract).
- Ability of alcoholic extract on corrosion inhibition of steel is higher than that of aqueous extract which is consistent with the results of the chemical study.
- Decrease in corrosion current Icorr. values by increasing the concentration of the extract, which associated with the change in the values Ecorr. to lower values especially at high concentrations.
- Increase in concentration of the inhibitor have an obvious effect on the corrosion current Icorr. and thus lower the corrosion rate which indicates the ability of extracts to inhibit the corrosion of steel.
- Tafel slopes (cathodic bc and anodic ba) for the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH in the presence of aqueous extract and alcoholic extract of *RC*

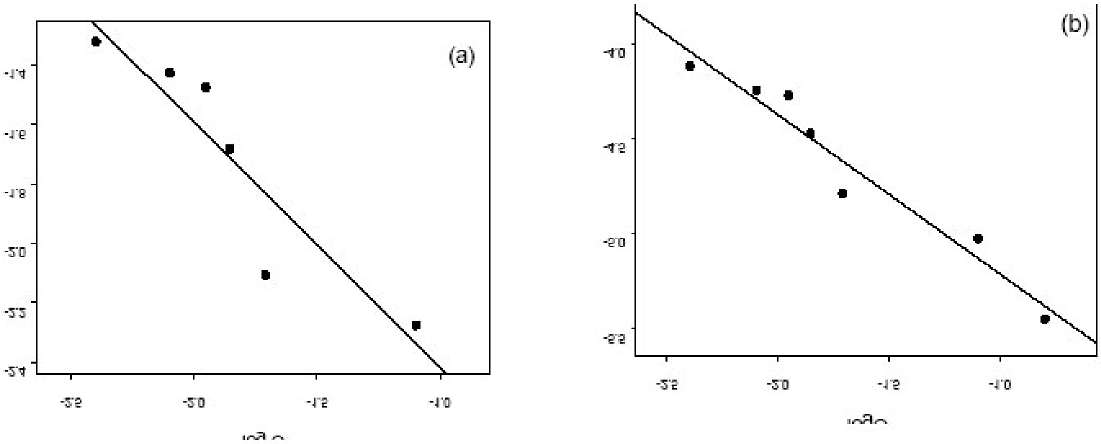


Fig. 3: Relationship between logarithm of concentration (logC) for *RC* aqueous extract in 2.0 M H_2SO_4 +10% EtOH against a) log R and b) log R' for steel corrosion at 30 °C

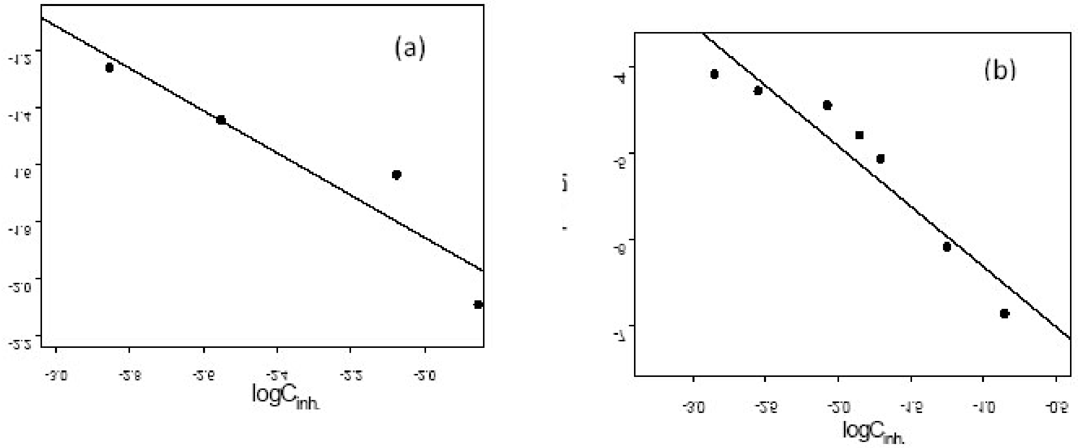


Fig. 4: Relationship between logarithm of concentration (logC) for *RC* alcoholic extract in 2.0 M H_2SO_4 +10% EtOH against a) log R and b) log R' for steel corrosion at 30 °C

plant was change in irregular form, and bc and ba values have lower values with increasing concentration of the extracts (aqueous and alcoholic) of *RC* plant, this means that the plant extracts under study works as mixed type inhibitors.

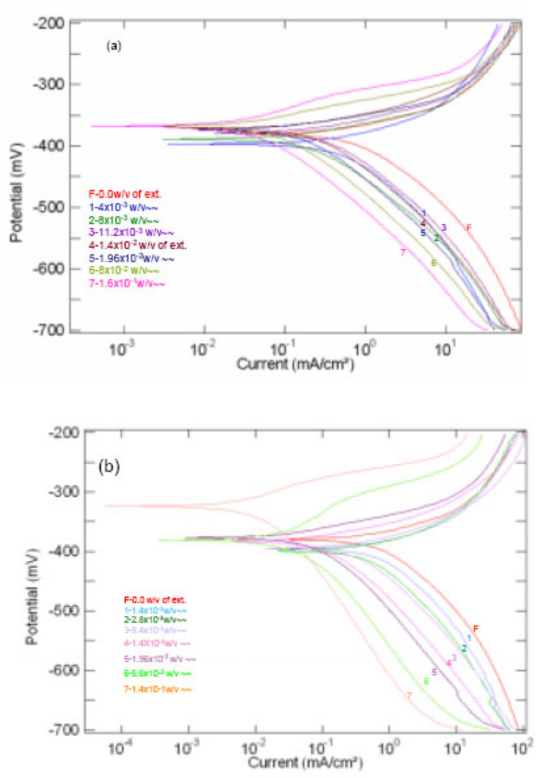


Fig. 5: Polarization curves for steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in absence and presence of different concentrations of *RC* plant a) aqueous extract and b) alcoholic extract at 30p C

Inhibition efficiency (%Inh.P) increase with increasing the concentration of the extracts of *RC* plant (from the application of equation (7)).

Impedance measurements (EIS)

Figs. (7 and 8) illustrate Nyquist diagrams for the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH in absence and presence of different concentrations of aqueous extract and / or alcoholic extract of *RC* plant at 30°C. It is clear from the figures that impedance curves often give a half circle, which indicates that the process of corrosion of steel under study are mainly controld by charge transfer resistance and the presence of aqueous extract and / or alcoholic extract of *RC* plant in H_2SO_4 acid solution does not affect the mechanism of metal dissolution, and the differences apparent attributed to the dispersion of the frequency. The value of charge transfer resistance obtained using the equation of Stern-Geary[27] (where the corrosion current obtained from electrical impedance at high and low frequencies), as suggested by Tsura and co-workers[28].

The values of the charge transfer resistance (Rct) and the percentage of inhibition efficiency (%Inh.Rct) were recorded in Tables (4 and 5), which show that the values of Rct increase with increasing the concentration of aqueous extract and / or alcoholic extract of *RC* plant, and therefore the

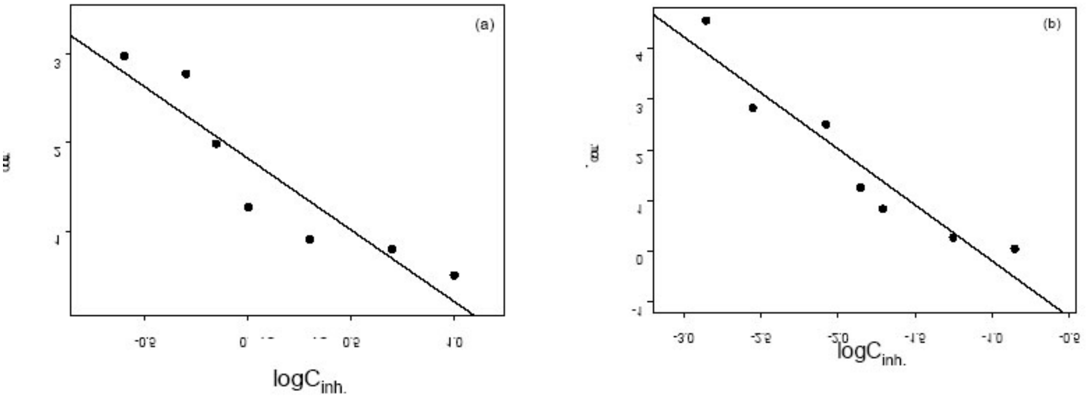


Fig. 6: Relationship between logarithm of concentration (log C) of *RC* plant a) aqueous extract and b) alcoholic extract in 2.0 M H_2SO_4 + 10% EtOH against Icorr. for steel corrosion at 30 °C

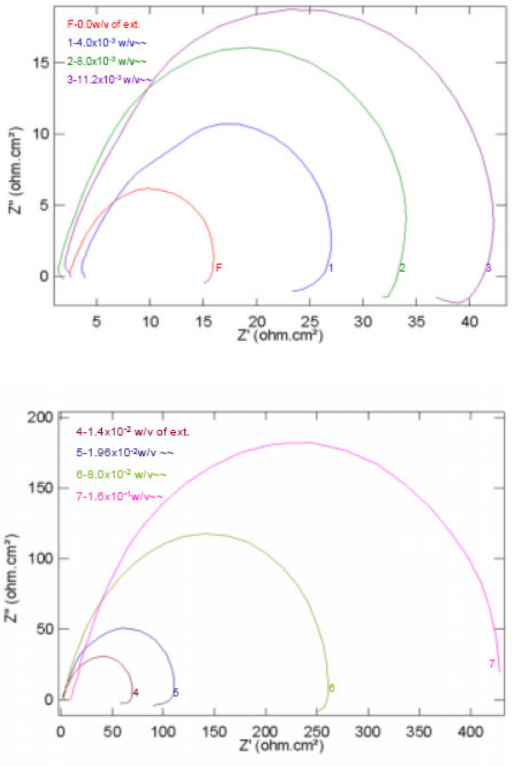


Fig. 7: Nyquist plots of steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in absence andpresence of different concentrations of *RC* aqueous extract at 30°C

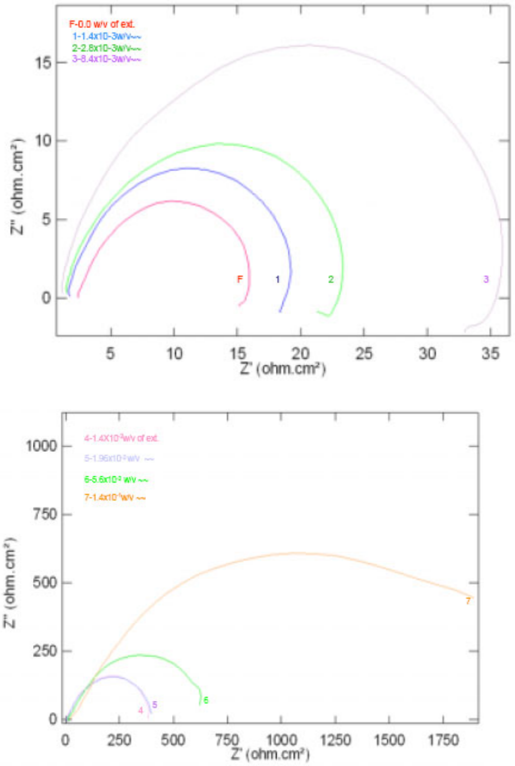


Fig. 8: Nyquist plots of steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in absence and presence of different concentrations of *RC* alcoholic extract at 30°C

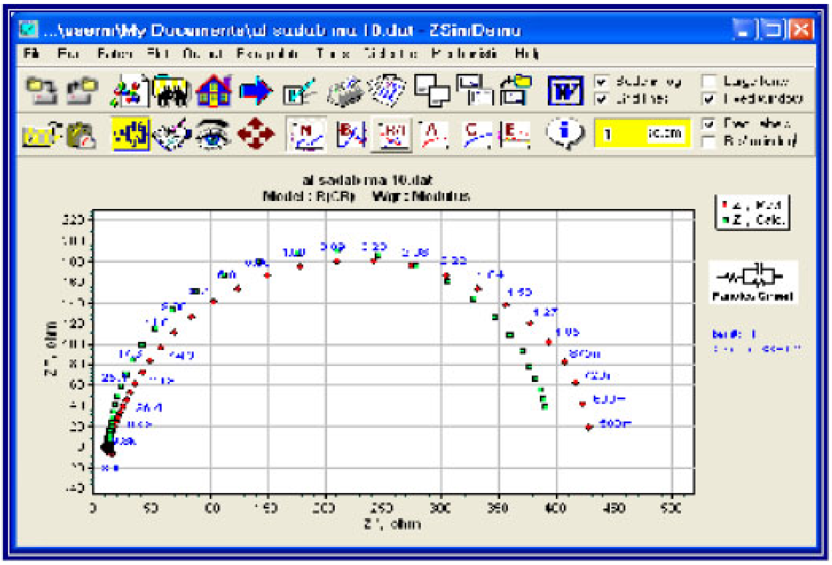


Fig. 9a: Circuit simulation proposed electrochemical impedance spectrum for steel corrosionin 2.0 M H_2SO_4 + 10% EtOH in presence of 1.6x10-1 w/v concentration of *RC* aqueous extract at 30°C

corrosion rate of steel sample will decrease in the solution under study, and increase the percentage of inhibition. The increase charge transfer resistance in the presence of the studied extracts is due to the remove of water molecules gradually through the adsorption of the components of aqueous extract and / or alcoholic extract of *RC* plant on steel metal surface, the %Inh.Rct from impedance measurements were calculated by the application of equation (8).

Examination of Tables (4 and 5), it is clear that there are differences noticeable in the inhibition efficiencies calculated from different methods (chemical and electrochemical methods), this difference is evident in the low concentrations of the extract, while the consistent results when high concentrations of aqueous extract and alcoholic extract of the *RC* plant, and also notes that %Inh.p from polarization measurements always higher than

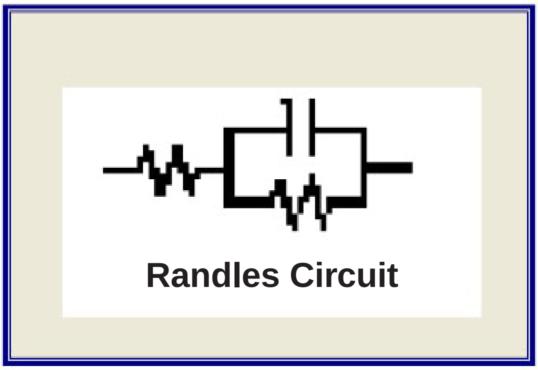


Fig. 9(b): Equivalent circuit model for steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in presence of 1.6x10^{-1} w/v of *RC* aqueous extract at 30°C (Randal equivalent circuit model)

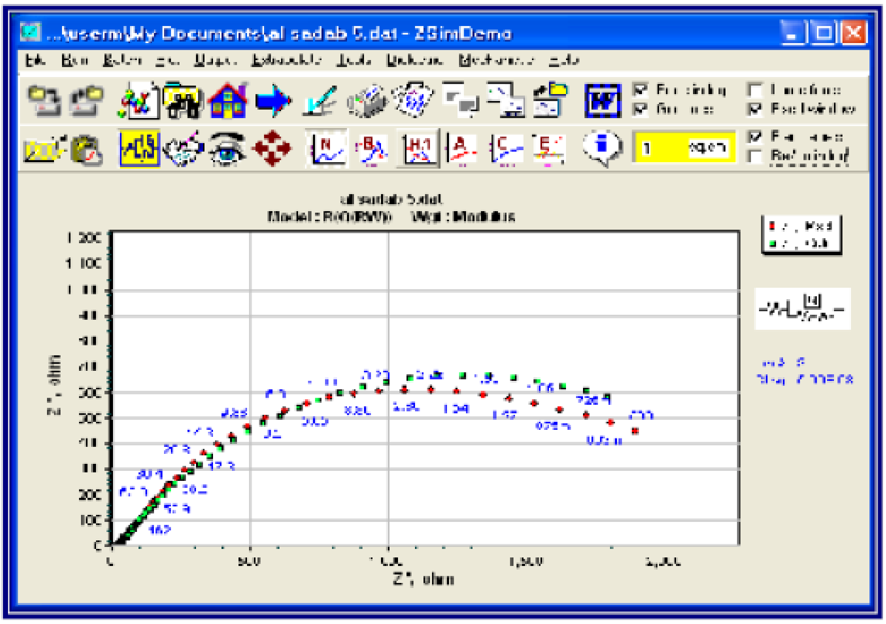


Fig. 10(a): Circuit simulation proposed electrochemical impedance spectrum for steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in presence of 1.6×10^{-1} w/v concentration of *RC* alcoholic extract at 30°C

those calculated from chemical measurements, and a good agreement in results at high concentrations of the extract, this attributed to an increase in condensation on the metal surface (an increase of adsorption molecules of aqueous extract and alcoholic extract of the *RC* plant on the surface of steel under study).

Comparing the results derived from chemical and electrochemical measurements for aqueous extract and / or alcoholic extract of *RC* plant was found that alcoholic extract gives inhibition efficiencies higher than that in the case of aqueous extract this is attributed to the nature of the materials extracted from tow solvents (water and alcohol), where give the inhibition percentage equal 100% at a concentration 1.6x10^{-1} w / v of aqueous extract and at a concentration 1.96x10^{-2} w /v of the alcoholic extract of *RC* plant. Figures (9 and 10) give Nuquist plots and electrical equivalent circuit at high and

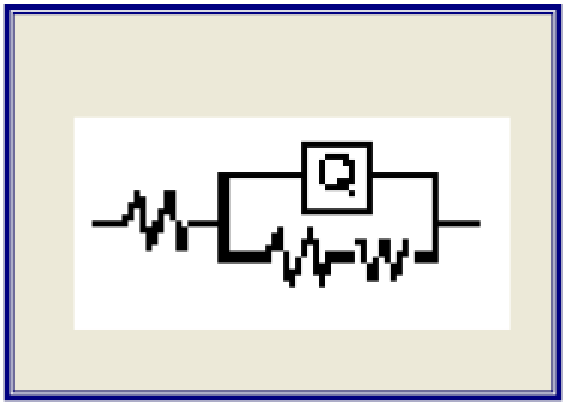


Fig. 10(b): Equivalent circuit model for steel corrosion in 2.0 M H_2SO_4 + 10% EtOH in presence of 1.6×10^{-1} w/v of *RC* alcoholic extract at 30°C (Randal equivalent circuit model)

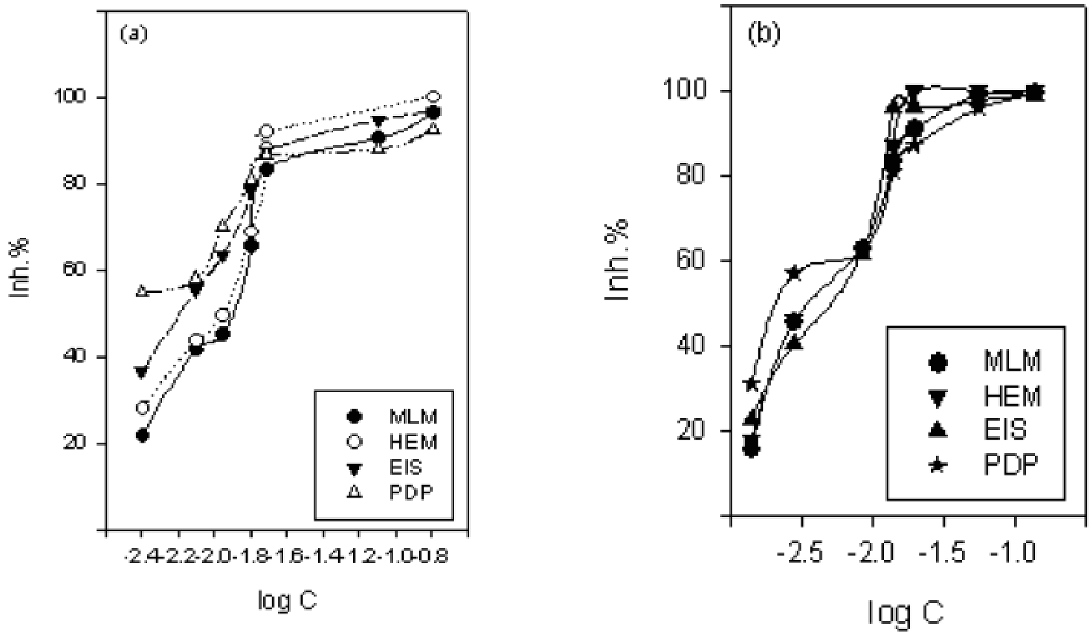


Fig. 11: The variation of inhibition efficiency (%Inh.) against log Cinh. of a) aqueous extract and b) alcoholic extract of *RC* plant for steel corrosion in 2.0 M H_2SO_4 at 30°C

low concentrations of aqueous extract and / or alcoholic extract of *RC* plant as a model.

Fig. (9) gives Nyquist plots (9a) and electrical equivalent circuit (9b) [RS (Cdl Rct)] for the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH in the presence of high concentration $1.6{\times}10^{-1}$ w / v of the aqueous extract of *RC* plant at 30°C, which it was emulated by simple Randall circuit as in Fig. (9b) which can be represented as follows [Rs (Cdl Rct)].

Also, Figure (10) shows Nyquist plots (10a) and electrical equivalent circuit (10b) for the corrosion of steel sample in 2.0 M H_2SO_4 containing 10% EtOH in the presence of the highest concentration of alcoholic extract ($1.4{\times}10^{-1}$ w / v) at 30°C, where give [RS (Q (Rct W))], it is clear from

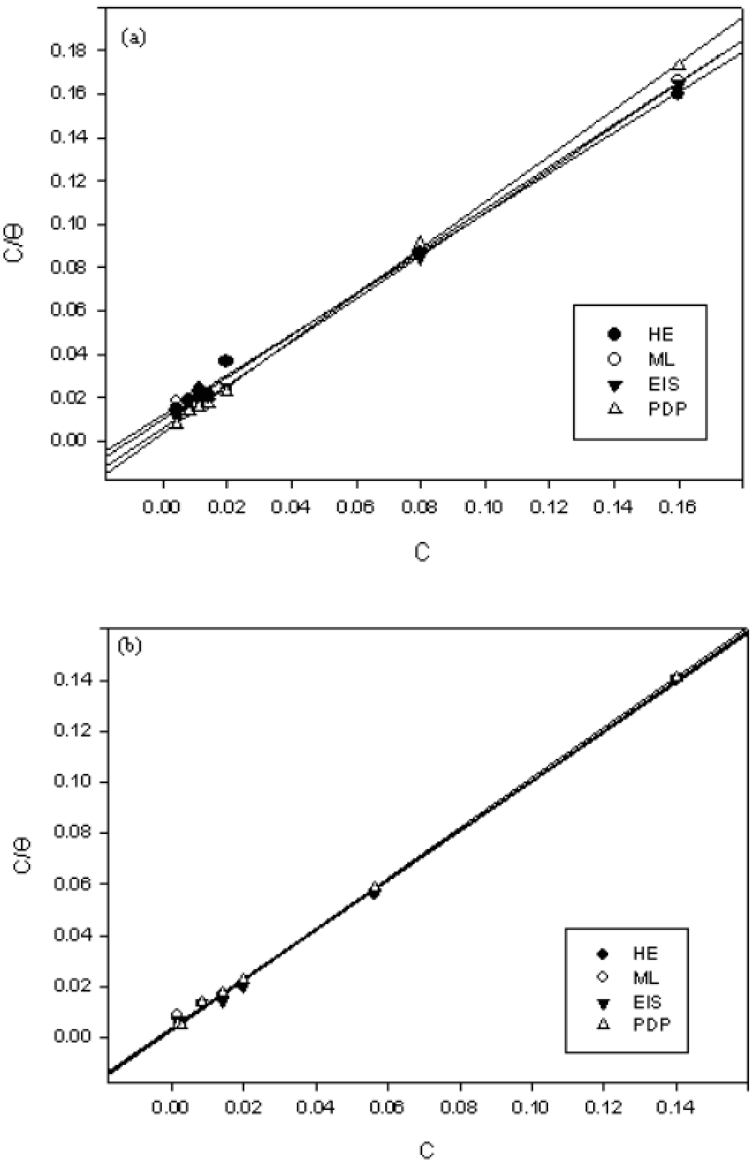


Fig. 12: The relation between C/ƒÁ against C for a) aqueous extract and b) alcoholic extract of *RC* plant for steel corrosion in 2.0 M H_2SO_4 + 10% EtOH at 30°C (Langmiur isotherm)

the Figure and the equivalent circuit that current diffusion control the process of steel corrosion inhibition.

Adsorption isotherms Figure (11) illustrates the relation between the percentage of inhibition (%Inh.) and the logarithm of the concentration (log Cinh.) of the extracts (aqueous and alcoholic) of *RC* plant for steel in 2.0 M H_2SO_4 containing 10% EtOH from chemical (HE and ML) and electrochemical (PDP and EIS) methods, which gives *S*-shape curves, this indicates that the aqueous extract and alcoholic extract of *RC* plant inhibit the corrosion of steel in H_2SO_4 through

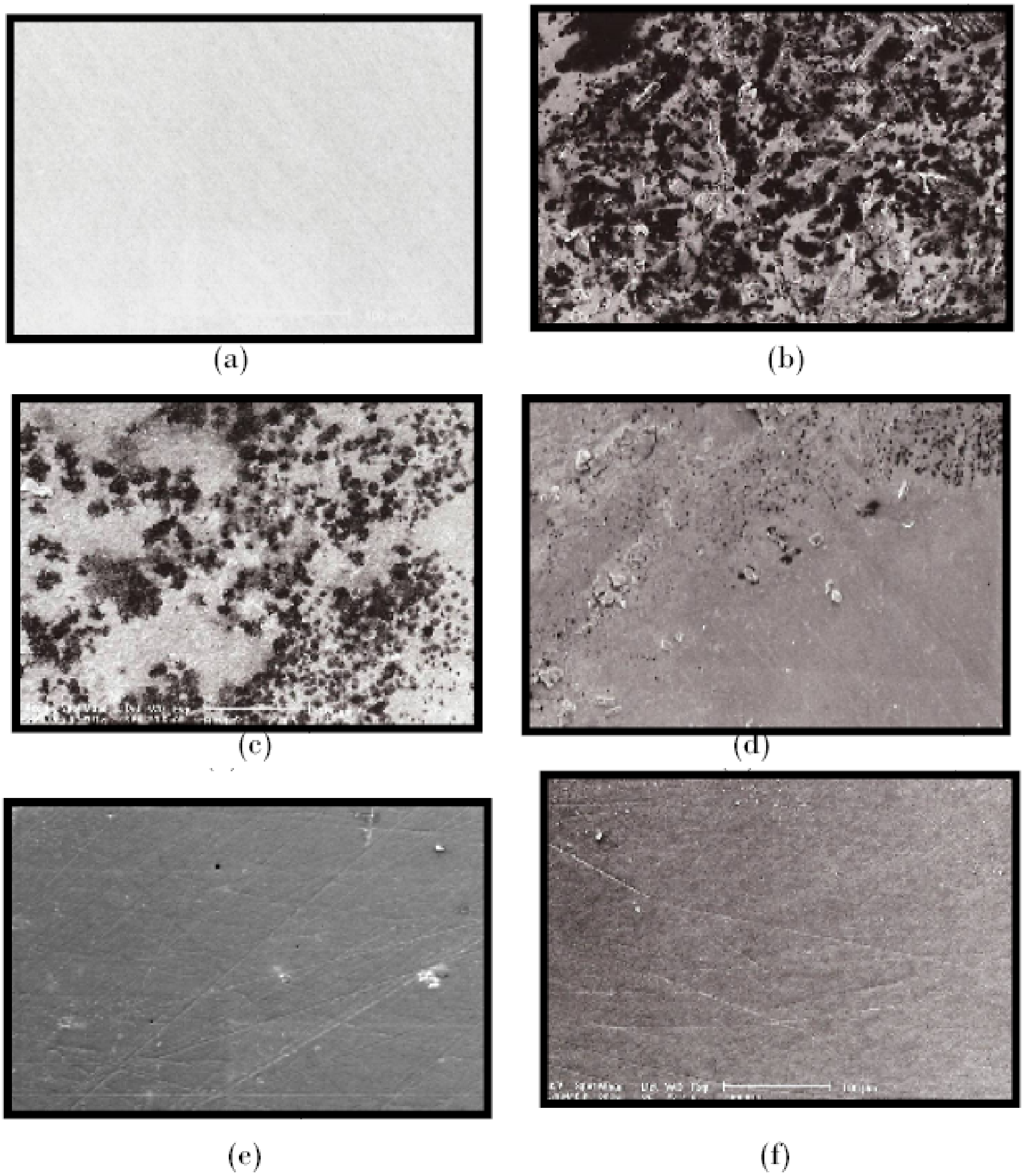

(a) (b)
(c) (d)
(e) (f)

Fig. 13: SEM of steel surface after 60 mints. of immersion in 2.0 M H_2SO_4 +10%EtOH in absence and presence of *RC* extracts a) sample as received (b) sample in free acid (c) 4×10^{-3} w/v, (e) 1.6 × 10^{-1} w/v of *RC* aqueous extract and (d) 8.4×10^{-3} w/v, f) 1.4x10-1 w/v of *RC* alcoholic extract at 30°C

adsorption of the components of the extract on the metal surface, and it is indicate that the adsorption occurs probably in two steps, because of their small molecules of *RC* plant where it is possible to adsorb of some small molecules on the surface of steel sample followed by adsorption of benzene compounds, which leads to the formation of Vanderfal bonds between the adsorbed molecules

Table 4: Electrochemical parameters and inhibition percentages of steel sample corrosion in 2.0 M H_2SO_4 +10% EtOH in absence and presence of different concentrations of *RC* aqueous extract at 30°C

Conc.	Polarization					Impedance		Inhibitions	
(w/c)	$-E_{corr}$ (mv)	b_a (V dec^{-1})	b_c (V dec^{-1})	$I_{coor.}$ (mA. cm^3)	$R_{corr.}$ (mmday^{-1})	$R_{sol.}$ (Ωcm^2)	$R_{ct.}$ (Ωcm^2)	%Inh.p	%Inh. R_{ct}
0.0	380.46	103.96	95.68	6.586	76.331	2.253	14.15	-	-
4.0×10^{-3}	401.24	67.00	134.37	2.979	34.52	4.279	22.31	54.77	36.57
8.0×10^{-3}	391.32	40.26	116.95	2.775	32.17	1.729	31.71	57.87	55.38
11.2×10^{-3}	378.84	40.62	136.61	1.988	23.04	2.81	38.77	69.81	63.51
1.4×10^{-2}	374.04	30.43	132.53	1.270	14.723	3.28	65.01	80.72	78.23
1.96×10^{-2}	373.21	23.74	54.07	0.907	10.51	2.241	112.2	86.23	87.39
8.0×10^{-2}	367.89	25.93	47.08	0.801	9.278	2.068	259.0	87.84	94.54
1.6×10^{-1}	366.65	28.11	41.26	0.504	5.843	1.093	421.3	92.38	96.64

Table 5: Electrochemical parameters and inhibition percentages of steel sample corrosion in 2.0 M H_2SO_4 +10% EtOH in absence and presence of different concentrations of *RC* alcholic extract at 30°C

Conc.	Polarization					Impedance		Inhibitions	
(w/c)	$-E_{corr}$ (mv)	b_a (V dec^{-1})	b_c (V dec^{-1})	$I_{coor.}$ (mA. cm^3)	$R_{corr.}$ (mmday^{-1})	$R_{sol.}$ (Ωcm^2)	$R_{ct.}$ (Ωcm^2)	%Inh.p	%Inh. R_{ct}
0.0	380.46	103.96	95.68	6.586	76.331	2.253	14.15	-	-
4.0×10-3	401.24	67.00	134.37	2.979	34.52	4.279	22.31	54.77	36.57
8.0×10-3	391.32	40.26	116.95	2.775	32.17	1.729	31.71	57.87	55.38
11.2×10-3	378.84	40.62	136.61	1.988	23.04	2.81	38.77	69.81	63.51
1.4×10-2	374.04	30.43	132.53	1.270	14.723	3.28	65.01	80.72	78.23
1.96×10-2	373.21	23.74	54.07	0.907	10.51	2.241	112.2	86.23	87.39
8.0×10^{-2}	367.89	25.93	47.08	0.801	9.278	2.068	259.0	87.84	94.54
1.6×10^{-1}	366.65	28.11	41.26	0.504	5.843	1.093	421.3	92.38	96.64

Table 6: The adsorption constants (Kads. and “Go ds.) obtained from Langmiur isotherm for *RC* aqueous extract in 2.0 M H_2SO_4+10% EtOH at 30°C

Method	Kads. (ml/gm)	Slope	ΔGo ds. a (k.J.ml.gm-1)	C.C%
HE	84.75	0.93	21.30	99
MS	94.34	0.97	21.57	99
EIS	140.94	0.99	23.07	99
PDP	277.78	1.07	24.29	99

especially since these compounds will be separated from the plant under study are polar materials with the ability of attraction with each other (Table 1).

It was illustrate from Fig. (12) that when applying the Langmuir equation:

$$\Theta = K\ C_{extracts}\ /\ 1+KC_{extract} \qquad ...(9)$$

$$C/\ \Theta = 1/K+C \qquad ...(10)$$

where C represents concentration of the extract, ƒΘ degree of coverage and K adsorption constant, that a straight lines was obtained with a slope close to unity equal to 0.9897 for the aqueous extract and 0.974 for alcoholic extract and this indicates that they follow Langmuir adsorption isotherm. The values of adsorption constant (Kads.) and the standard free energy of adsorption (”Goads.) which obtained from the application of the equation: 11

$$K = 1/55.5\ \exp\ (-\Delta G^{o}_{ads.}\ /\ RT) \qquad ...(11)$$

were recorded in Tables (6 and 7) for both aqueous extract and alcoholic extract, respectively. It is show that the values of ”Goads. have negative sign indicate to the spontaneous strong adsorption of *RC* plant extracts, and this appears from the high values of the inhibition efficiencies (%Inh.).

Microstructure Study of Steel Surface by SEM

Figure (13) shows the electronic microscopy imaging for steel sample in 2.0 M H_2SO_4 containing 10% EtOH for 60 minutes immersion at 30oC in the absence and the presence of aqueous extract and alcoholic extract of *RC* plant. Figure (13a) shows electronic imaging of the clean surface of steel sample before immersing in acid solution, where it shows the homogeneity of the surface as mentioned above. As shown in Figure (13b) the effect of adding a solution 2.0 M H_2SO4 containing 10% EtOH on a steel sample at 30oC, where noted that there is corrosion with holes deep and regular surface of steel in the absence of extracts of *RC* plant.

As shown in Figures (13c and 13d) electronic microscopy imaging for steel surface in

Table 6: The adsorption constants ($K_{ads.}$ and $\Delta G^o\ d_{s.}$) obtained from Langmiur isotherm for *RC* aqueous extract in 2.0 M H_2SO_4+10% EtOH at 30°C

Method	Kads. (ml/gm)	Slope	ΔGo ds. a (k.J.ml.gm^{-1})	C.C%
HE	84.75	0.93	21.30	99
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Table 6: The adsorption constants ($K_{ads.}$ and $\Delta G^o\ d_{s.}$) obtained from Langmiur isotherm for *RC* aqueous extract in 2.0 M H_2SO_4+10% EtOH at 30°C

Method	Kads. (ml/gm)	Slope	ΔGo ds. a (k.J.ml.gm^{-1})	C.C%
HE	293.26	0.97	24.43 99	
MS	235.29	0.97	23.88 99	
EIS	316.46	0.98	24.62 99	
PDP	292.40	0.98	24.42 98	

2.0 M H_2SO_4 containing 10% EtOH in the presence of low concentration of *RC* plant extracts under study at 30°C, it is clear from the figures that at low concentration of the aqueous extract ($4x10^{-3}$ w/v) and alcoholic extract (8.4x10-3 w/v) of *RC* plant the existence of holes on the surface of steel, but less than those in the case of pure H_2SO_4 acid, and this indicates that the formation of a protective thin and porous layer of *RC* plant molecules on steel surface. Whereas the Figs.(13e and 13f) illustrates the effect of increasing the concentration of aqueous (1.6×10^{-1} w/v) and alcoholic ($1.4x10^{-1}$ w/v) extracts of *RC* plant to inhibit the corrosion of steel, which shows the formation of non-porous layer on the surface of steel metal, this layer indicate to the adsorption of the components of extract with the disappearance of holes. This is consistent with previous results that were obtained from the chemical and electrochemical measurements. As shown in Figures (c and e) and Figures (d and f) that the alcoholic extract gave the highest degree of protection than the aqueous extract which was reflected in the homogeneity of the surface more in the case of alcoholic extract.

When the comparison between the aqueous extract and alcoholic extract of *RC* plant the following appears:

- Corrosion rates of steel sample in 2.0 M H2SO4 containing 10% EtOH decrease with increasing the concentration of aqueous extract and alcoholic extract of *RC* plant at 30°C (i.e., increasing the inhibition efficiency).
- The results of polarization measurements shows that the aqueous extract and / or alcoholic extract of *RC* plant act as mixed inhibitors.
- The results of impedance measurements gives semi-circle which indicates that the process of corrosion of steel under study in the presence of aqueous extract and alcoholic extract of *RC* plant are mainly submit to the charge transition process with the exception of concentration $1.4x10^{-1}$ w/v of alcoholic extract which the equivalent circuit shows to the formation of diffusion layer.
- The alcoholic extract of *RC* plant gives inhibition efficiency higher than that of aqueous extract this is due to the nature of the materials derived from *RC* plant by the two solvents.
- The results of the SEM of steel surface shows the cover of the surface is clear at the high concentrations of aqueous extract and alcoholic extract of *RC* plant. And it was made clear in the case of alcoholic extract.

CONCLUSION

From the experimental results obtained in the present study, the following conclusions could be drawn:

- Aqueous extract and alcoholic extract of *Ruta chalepensi (RC)* plant act as mixed inhibitors for steel corrosion in H_2SO_4 solution.
- Inhibition efficiency (%Inh.) increased with increasing the concentration of the aqueous extract and alcoholic extract of *RC* plant.
- The calculated values of “*Gp ads.*were negative which suggested that aqueous and /or alcoholic extract of *RC* plant was spantenuos and strongly adsorbed on steel surface.
- The adsorption process for aqueous and / or alcoholic extract of *RC* plant followed the Langmuir adsorption isotherm.

REFERENCES

1. G. Schmitt, Br. *Corrosion*, **19**(4): 166 (1984).
2. G. Trabanelli and V. Corassiti, Advances in Corrosion Science and Technology, Ed. M.G. Fontana and R. W. Stachle, Plenum Press, New York, **1**: 147 (1991).
3. A. Tosun and M. Ergun, Protection of Corrosion of Carbon Steel by Inhibitors in Chloride Containing Solutions, G. U. *Journal of Science*, **19**(3): 149-154 (2006).
4. R. Grawal and T. Namboodhiri, The Inhibition of Sulphuric Acid Corrosion of 410 Stainless Steel by Thioureas, *Corros. Sci.*, **30**(1): 37-

52 (1990).

5. E. Lisac, S. Prdbrscek and T. Soric, Non- Toxic Organic Zinc Corrosion Inhibitors in Hydrochloric Acid, *J. App. Electrochem*., **24**: 799(1994) .
6. M. Hukovic, R. Babic and Z. Brinic, *J. App. Electrochem.,* **24**: 325 (1994) .
7. A. El- Etre, Inhibition of Corrosion of Aluminum Using Vanillin, *Corros. Sci.,* **43**: 1031-1039 (2001) .
8 S. S. Abd El-Rehim, H. H. Hassan and M. A. Amin, Corrosion Inhibition of Aluminum by 1, 1 (Lauryl Amido) Propyl Ammonium Chloride in HCl Solution, *Mater. Chem. Phys.,* **70**: 64-72 (2001).
9. S. T. Arab and A. M. Al-Turkustani, The Effect of Temperature on The Inhibition of the Acid Corrosion of Mild Steel by some Sulfomium Bromide Derivatives, *Int. J.Chem*., **12**(4): 249-268 (2002).
10. M. Henthorne, Materials Selection for Corrosion Control, *Chemical Eng.,* **1**: 1139-1146 (1971).
11. E. Chaieb, A. Bouyanzer, B. Hammouti and M. Benkaddour, Inhibition of the Corrosion of Steel in 1.0 M HCl by Eugenol Derivatives, *Appl. Surf. Sci*., **246:** 199-206 (2005).
12. M. Ibrahim, H. Abd El- Hakeem and E. El-Krisy, Inhibitors for Acid Pickling of Steel from *Citrus Fruit* Waste Products, 3rd National Meeting of Chemists, King Fahad Univ., 261-267 (1989).
13. N.O. Eddy and E.E. Ebenso, *African J. Pure Appl. Chem*. **2**(6): 1 (2008).
14. N.O. Eddy and S. A. Odoemelam*, Pigment and Resin Technol.* **38**(2): 111 (2009).
15. A. O. Odiongenyi, S. A. Odoemelam and N. O. Eddy, *Portugaliae Electrochimica Acta* **27**(1): 33 (2009).
16. A.Y. El-Etre, *Corros. Sci*. **45:** 2485 (2003).
17. A.Y. El-Etre, M. Abdullah and Z.E. El-Tantawy, *Corros. Sci*. **47**: 385 (2005).
18. A.Y. El-Etre, *Appl. Surface Sci*. **252**: 8521 (2006).
19. E.E. Ebenso, N.O. Eddy and A.O. Odiongenyi, *Afri. J. Pure and Appl. Chem.* **2:** 107 (2008).
20. N.O. Eddy, P. Ekwumemgbo and S.A. Odoemelam, Inter. *Journal Physical Sci*. **3**: 1 (2008) .
21. N.O. Eddy, S.A. Odoemelam and A.O. Odiongenyi, J. Appl. Electrochem. DOI 10.1007/s10800-008-9731 (2008).
22. N.O. Eddy, S.A. Odoemelam and N.W. Akpanudoh, *J. Chem. Technol.* **4**: 1 (2008).
23. S.A. Odoemelam and N.O. Eddy, *J. Surface Sci. Technol.* **24**: 1 (2008).
26. E.E. Ebenso, *Bull. Electrochem.* **19**: 209 (2003).
27. M. Stern and L. Geary, *J. Electrochemical. Soc*., **104**: 56 (1957).
28. T. Tsura, S. Haruyama and B. Gijutsu, *J. Jpn. Soc. Corros. Eng.,* **27**: 570 (1978) .