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Inhibitive Action of Aqueous Extract of *Zygophyllum Album L* Leaves on the Corrosion of Carbon Steel in Hydrochloric Acid Solution

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ABSTRACT

Corrosion inhibition of mild steel in hydrochloric acid solutions by the extract of Zygophyllum Album L (ZPAL) leaves has been studied using gravimetric measurements, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. Inhibition efficiency was found to increase with the concentration of the inhibitor to attain 89 % at 1000 mg/L of ZPAL. Polarization curves reveal that extract of Zygophyllum Album L acts as mixed type inhibitor. Changes in impedance data were indicative of the extract adsorption on the metal surface, leading to the formation of a protective film. The thermodynamic study shows that adsorption of ZPAL proceeds via physisorption mode and obeys the Langmuir adsorption isotherm.

Keywords: *Corrosion, Green inhibitor, Polarization, EIS, Carbon steel.*

INTRODUCTION

Corrosion of metals is a very common problem with economic implications costing billions of dollars every year. Corrosion inhibition is required by many industries, for example oil and gas exploration and production, petroleum refining, chemical manufacturing, and the product additive industries [1]. The use of corrosion inhibitors is one of the best economical and practical methods to prevent or to reduce corrosive attack on metals. Inhibitors are chemicals either synthetic or natural that often work by adsorption on the metal surface and the formation of a protective film. Synthetic compounds with inhibitive properties have been widely investigated in the literature [2–5]. However, interest in using natural products as corrosion inhibitors increased substantially over the last decade because of cost, toxicity, availability, and eco-friendliness considerations. Various natural products have been reported to be very good corrosion inhibitors [6–10], probably due to the presence of alkaloids and flavonoids [11-13].

In continuation of our work on the development of green corrosion inhibitors [10, 14], we report herein the inhibiting effect of *Zygophyllum Album L* (ZPAL) leaves aqueous extract on the corrosion of carbon steel in acidic medium. *Zygophyllum album L* is a shrubby plant in Zygophyllaceae family. This plant is widespread in southern Algeria where it is commonly known as "*Agaya*". Local population used it in traditional medicine for its anti-spasmolytic, anti-histaminic, antihyperlipidemic, antidiarrheal and anti-inflammatory effects. Its inhibition effect on the corrosion of C-steel in 1M HCl solution has been studied using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods.

EXPERIMENTAL DETAILS

Solutions and Materials

1M HCl solutions were prepared by dilution of analytical reagent grade 37% HCl with distilled water and were used as the corrosive media.

Tests were performed on C-steel of the following composition (wt.%): 0.370% C, 0.680% Mn, 0.230% Si, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu and the remainder iron (Fe).

Zygophyllum Album L was collected from Bechar (South-west of Algeria). Dried *ZPAL* leaves (10g) were soaked in 1M HCl solution (500 mL) and refluxed for 5 h. The aqueous solution was then filtered and concentrated to 100 mL. This concentrated solution was used to prepare, by dilution method, extract solutions of concentrations in the range 200 mg L^{-1} to 1000 mg L^{-1} [15].

Weight loss measurements

Steel specimens for weight loss measurements were 13 mm by 12 mm by 1 mm. Prior to each experiment, these samples were polished with emery paper (grade 600, 800, 1000 and 1200). Each run was carried out by complete immersion of clean weighed specimens at an inclined position in a glass vessel containing 100 mL of the test solution at different temperatures. After 3 h of immersion in 1M HCl with and without addition of ZPAL extract at different concentrations, the specimen was withdrawn, rinsed with double distilled water, degreased with acetone, dried and weighed using an analytical balance accurate to 0.01 mg. All experiments were performed in triplicate and the mean value of the weight loss was calculated.

Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy were conducted in a 500mL double-walled thermostated electrolytic cell (CEC/TH-Radiometer) with a conventional three-electrode cell assembly, using a PGZ301 potentiostat piloted by VoltaMaster 4 software. Platinum disc was used as a counter-electrode (CE) and a saturated calomel electrode (SCE) as a reference electrode. The latter was connected to the cell through a Luggin's capillary. The working electrode (WE) was in the form of a disc cut from the carbon steel under investigation and embedded in a Teflon rod with an exposed area of 0.5 cm^2. Before use, the WE were polished with emery papers (from 600 to 1200 grades), washed with distilled water, degreased by acetone, rinsed with double distilled water and dried at room temperature. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from -700 to -300 mV versus SCE at a scan rate of 0.5

mVs^{-1}. Before all experiments, the WE were immersed in 200 mL of freshly prepared solution for 1 h until a steady state open-circuit potential (E_{ocp}) was obtained. All experiments were carried out at constant temperatures, 30, 40, 50 and 60 ± 0.1°C. Impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz to 10 MHz, with a signal amplitude perturbation of 10 mV. Impedance parameters were calculated using Z-View software, version 2.80, 2002, Scribner Associates Inc.

RESULTS AND DISCUSSION

Weight loss measurements

The weight loss was used to calculate the corrosion rate in milligrams per square centimeter per hour. The corrosion rate (W_{corr}) is calculated using the following equation:

$$W_{corr} = \frac{\Delta m}{S \times t} \qquad (1)$$

where Δm is the average weight loss, S the total area, and t the immersion time.

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of steel for different concentrations of ZPAL extract in 1M HCl at 30°C after 3 h of immersion are given in table 1.

Table-1: Corrosion parameters obtained from weight loss measurements for carbon steel in 1M HCl containing various concentrations of ZAPL extract at 303 K.

Conc. (mg L^{-1})	W_{corr} (mg cm^{-2} h^{-1})	θ	E_w (%)
Blank	0.777	-	-
100	0.253	0.6742	67.42
200	0.176	0.7731	77.31
400	0.143	0.8163	81.63
600	0.092	0.8811	88.11
800	0.091	0.8829	88.29
1000	0.088	0.8871	88.71

The inhibition efficiency ($E_w\%$) is determined as follows:

$$E_w\% = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

where W_0 and W are values of the corrosion rate with and without the inhibitor, respectively.

It can be seen from table 1 that the corrosion rate (W_{corr}) decreases while the inhibition efficiency (E_w%) increases with increasing inhibitor concentration reaching a maximum value of 88.71 % at a concentration of 1000 mg L^{-1}.

This behavior can be attributed to the adsorption of the inhibitor molecules on the metal surface, as the inhibitor concentration increases, leading to an increase of the surface coverage θ (E_w%/100). We can conclude that ZPAL extract is a good corrosion inhibitor for mild steel in 1M HCl solution.

Potentiodynamic polarization

Polarization curves of the carbon steel in 1M HCl solutions without and with addition of different concentrations of ZPAL are shown in figure 1. This figure shows the cathodic and anodic polarization curves of mild steel in 1M HCl blank solution and in the presence of different concentrations of ZPAL. Both anodic and cathodic currents were inhibited when ZPAL concentration increases. This result shows that the addition of ZPAL inhibitor reduces anodic dissolution and also retards the hydrogen evolution reaction.

Table 2 gives the values of kinetic corrosion parameters as the corrosion potential E_{corr}, corrosion current density I_{corr}, Tafel slopes β_c and β_a, and the corresponding inhibition efficiency for the corrosion of mild steel in 1M HCl with different concentrations of ZPAL.

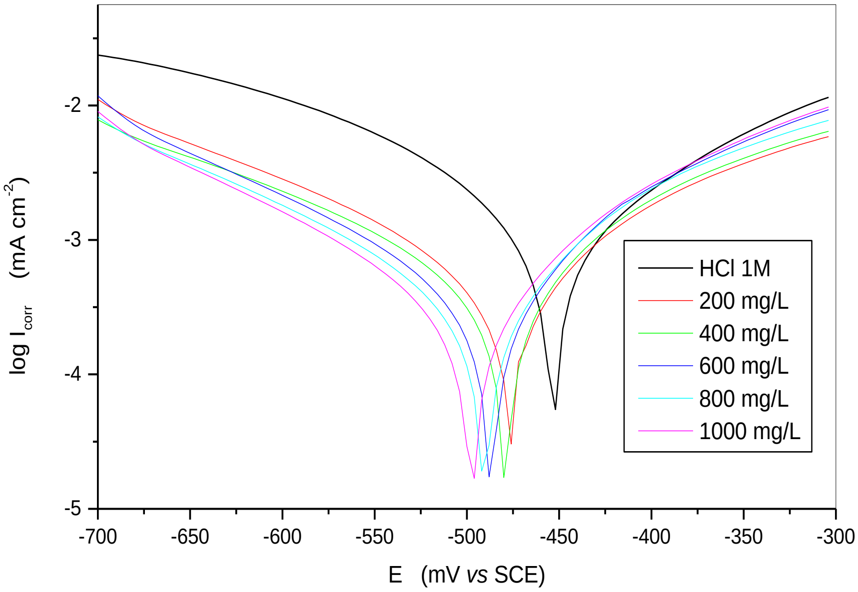

Figure-1: Potentiodynamic polarization curves for carbon steel in 1M HCl containing different concentrations of ZPAL at 303 K.

The corrosion current densities were estimated by Tafel extrapolation of the cathodic curves to the open circuit corrosion potentials. Inhibition efficiency (E_p%) was calculated using the expression:

$$E_p\% = \frac{I_{(uninh)} - I_{(inh)}}{I_{(uninh)}} \times 100 \qquad (3)$$

where $I_{(uninh)}$ is the corrosion current density in uninhibited acid and $I_{(inh)}$ is the corrosion current density in inhibited acid.

Table-2: Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of carbon steel in 1M HCl containing different concentrations of ZPAL extract at 303 K.

Conc. **(mg L^{-1})**	**-E_{corr}** **(mV *vs* SCE)**	**I_{corr}** **(mA cm^{-2})**	**-β_c** **(mV dec^{-1})**	**β_a** **(mV dec^{-1})**	**E_p** **(%)**
Blank	456	1.352	132.4	117.0	-
200	473	0.315	126.0	98.5	76.67
400	479	0.275	121.6	95.6	79.63
600	488	0.175	118.4	89.0	87.04
800	491	0.162	119.0	90.7	88.00
1000	499	0.154	114.9	86.8	88.59

From table 2, it is clear that the I_{corr} values decrease with increasing inhibitor concentration. The values of inhibition efficiency (E_p%) increase with inhibitor concentration reaching a maximum value (88.59%) at 1000 mg L^{-1}. The addition of ZPAL produces slight changes in the values of E_{corr} and cathodic Tafel slope. This indicates that the adsorbed molecules of ZPAL do not affect the mechanism of hydrogen evolution [17]. This result indicated that ZPAL act as a mixed type inhibitor for the corrosion of C-steel. The values of inhibition efficiency determined using potentiodynamic polarization are in good agreement with those obtained from Weight loss measurements.

Electrochemical impedance spectroscopy

Nyquist plots of steel in inhibited and uninhibited acidic solution containing various concentrations of *ZPAL* are shown in figure 2.

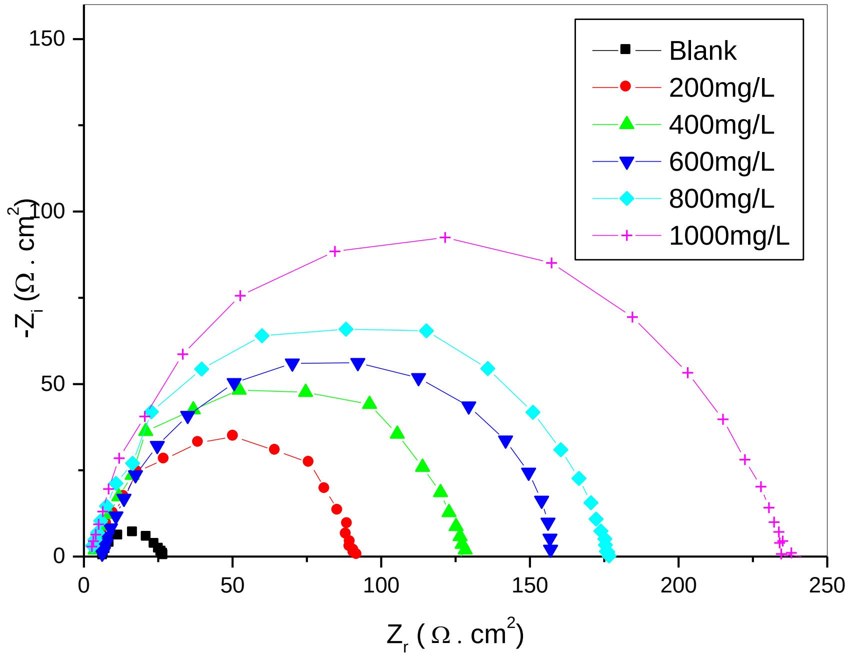

Figure-2: Nyquist plots recorded for carbon steel in 1M HCl without and with various concentrations of ZPAL at 303 K.

The impedance diagrams obtained are not perfect semicircles and the difference was attributed to frequency dispersion [18]. The fact that impedance diagrams have a semicircular appearance shows that a charge transfer process controls the corrosion of steel. The equivalent circuit model employed for this system is presented in figure 3.

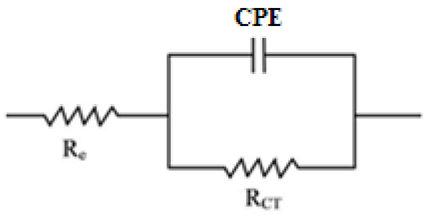

Figure-3: The electrochemical equivalent circuit used to fit impedance spectra obtained for ZAPL in 1M HCl.

R_e is the resistance of the solution; R_{ct} reflects the charge transfer resistance and CPE the constant phase element. Values of the charge transfer resistance R_{ct} were obtained from these plots by determining the difference in the values of impedance at low and high frequencies as suggested by Tsuru [19]. The value of capacitance, C_{dl}, can thus be calculated for a parallel circuit composed of a CPE (Q) and a resistor (R_{ct}), according to the following formula [20, 21]:

$$C_{dl} = (Q \times R_{ct}^{1-n})^{1/n} \qquad (4)$$

Inhibition efficiency (E_R %) is estimated using the relation:

$$E_R\% = \frac{R_{(inh)} - R_{(uninh)}}{R_{(inh)}}\ x\ 100 \qquad (5)$$

where $R_{(inh)}$ and $R_{(uninh)}$ are the charge transfer resistance values without and with inhibitor, respectively.

Table 3 gives the values of the charge transfer resistance R_{ct}, double-layer capacitance C_{dl}, and inhibition efficiency (E_{Rct}) obtained from the above plots.

Table 3. Impedance parameters and inhibition efficiency for the corrosion of mild steel in 1M HCl containing different concentrations of ZAPL extract at 303 K.

Conc. (mg/L)	**R_{ct} (Ω cm^2)**	**n**	**Q ($s^n\Omega^{-1}cm^{-2}$)**	**C_{dl} (μF cm^{-2})**	**E_R (%)**
Blank	25.0	0.80	6.5×10^{-4}	231.51	-
200	88.4	0.84	1.6×10^{-4}	70.64	71.72
400	124.7	0.85	1.3×10^{-4}	65.25	79.95
600	153,5	0.85	1.2×10^{-4}	61.05	83.71
800	173.1	0.86	8.9×10^{-5}	52.02	85.56
1000	231.6	0.87	9.1×10^{-5}	51.32	89.21

From this table, it can be seen that the R_{ct} values increase with inhibitor concentration and consequently the inhibition efficiency increases to 89.21% at 1000 mg L^{-1}. In fact, the presence of ZPAL is accompanied by the increase of the value of R_{ct} in acidic solution confirming a charge-transfer process mainly controlling the corrosion of C-steel. Values of double-layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of C_{dl}. The decrease in C_{dl} is due to the adsorption of the inhibitor on the metal surface leading to the formation of film or complex from acidic solution [22].

Results obtained from impedance measurements were in good agreement with those obtained from corrosion weight loss and polarization curves tests.

Effect of temperature

The effect of temperature on the inhibition efficiency, in the temperature range 303-333 K, in 1M HCl, was studied using gravimetric experiments in the absence and presence of 1000 mg L^{-1} of inhibitor after 3 h of immersion time. The variation in inhibition efficiency and surface coverage with temperature is shown in Table 4. The data show that inhibition efficiency of the extract decreases with increasing temperature, which may be attributed to a possible shift of the adsorption–desorption equilibrium toward desorption of the already adsorbed inhibitor. This result supports the idea that the adsorption of the extract components on the steel surface may be physical in nature.

Table-4: Effect of temperature on inhibition efficiency of 1000 mg L^{-1} ZPAL extract in 1M HCl solution during corrosion of C-steel for 3-h immersions.

Temperature (K)	**W_{corr}** (mg cm^{-2} h^{-1})		**θ**	**E** (%)
	HCl	**Extract**		
303	0,777	0,0883	0,8864	88,64
313	1,265	0,1572	0,8758	87,58
323	1,719	0,4257	0,7524	75,23
333	2,903	1,0185	0,6491	64,91

Figure 4 presents the plots of the natural logarithm of the corrosion rates (W_{corr}) versus 1/T, for 1M solution of hydrochloric acid, without and with addition of ZPAL extract. Straight-lines with the linear regression coefficient (R^2) high to 0.995 are obtained, indicating that the corrosion of steel in hydrochloric acid without and with ZPAL extract follows the Arrhenius equation.

The values of the slopes of these straight-lines permit the calculation of the Arrhenius activation energy, E_a, according to equation (6):

$$log\, W_{corr} = -\frac{E^*_a}{RT} + A \qquad (6)$$

where *R* is the universal gas constant and *A* is the Arrhenius factor. The calculated values of E_a are 35.42 kJ mol^{-1} (blank) and 69.29 kJ mol^{-1} (ZPAL). This result shows that the addition of ZPAL extract to the acid solution increases the activation energy. The increase of E_a in the presence of the inhibitor indicates physical adsorption or weak chemical bonding between the molecules of this inhibitor and the carbon steel surface [23].

An estimate of the heat of adsorption (Q_{ads}) was obtained from the trend of surface coverage with temperature as follows [24–26]:

$$Q_{ads} = 2.303 log\left\{\left(\frac{\theta_2}{1-\theta_1}\right) - \left(\frac{\theta_1}{1-\theta_2}\right)\right\} \times \frac{T_1\, T_2}{T_2 - T_1} \qquad (7)$$

where θ_1 and θ_2 the degree of surface coverage at temperatures T_1 and T_2, respectively. The negative values of heats of adsorption (Q_{ads} = -7.95 kJ mol^{-1}) indicate that the degree of surface coverage decreased with rise in temperature, again, suggesting physical adsorption mechanism [24–27].

The enthalpy of activation (ΔH_a) can be obtained from Eyring-type equation (8):

$$log\frac{W_{corr}}{T} = -\frac{\Delta H_a}{RT} + A' \qquad (8)$$

A plot of log (W_{corr}/T) versus *1/T* gave straight lines, of slope of $-\Delta H_a/R$, as shown in Figure 5. The ΔH_a values for the corrosion reaction in the absence and presence of 1000 mg L^{-1} of ZPAL extract are 32.79 and 66.67 kJ/mol, respectively. The positive sign of enthalpies ΔH_a reveals the endothermic nature of dissolution of C-steel, indicating that dissolution of C-steel is difficult [28].

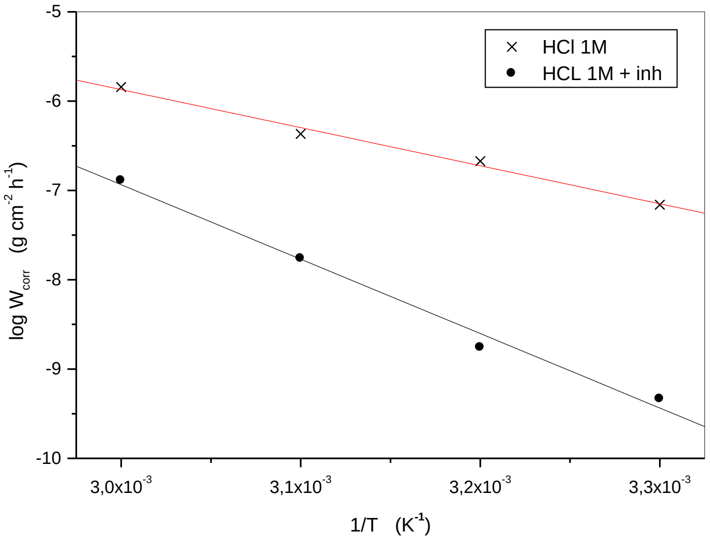

Figure-4: Arrhenius plots for C-steel corrosion rates (W_{corr}) in 1M HCl in the absence and presence of 1000 mg L^{-1} of ZPAL extract.

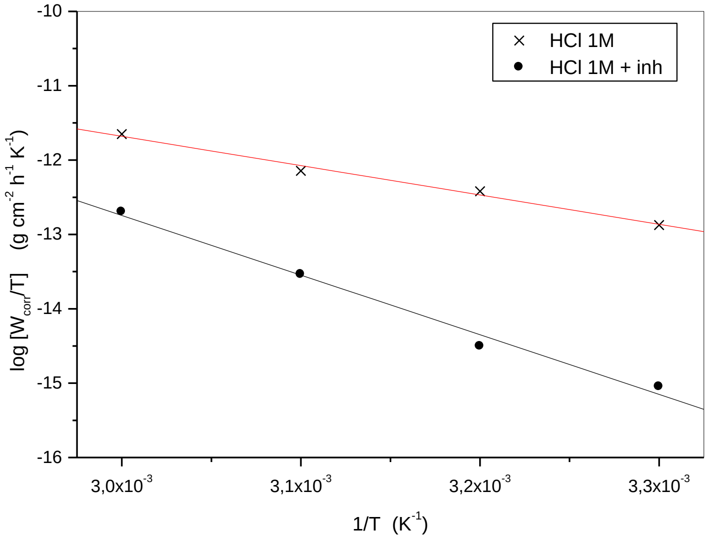

Figure-5: log (W_{corr}/T) *vs* 1/T for C-steel dissolution in 1M HCl in the absence and presence of 1000 mg L^{-1} ZPAL extract.

Adsorption isotherm

To understand the mechanism of corrosion inhibition, the adsorption behavior of the inhibitor adsorbed on the metal surface must be known. If simple adsorptive behavior is assumed for ZPAL, a direct relationship between inhibition efficiency and surface coverage takes place. Weight loss data were used to evaluate the surface coverage values, which are given by equation (9) [29]:

$$\theta = 1 - \frac{W}{W_0} \qquad (9)$$

where W_0 and W are the values of the corrosion rate with and without inhibitor, respectively.

Correlation between surface coverage (θ) and the concentration of the inhibitor (C_{inh}) can be represented by the Langmuir adsorption isotherm [30]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (10)$$

where θ is the degree of coverage on the metal surface, C_{inh} is the concentration in the electrolyte and K_{ads} is the equilibrium constant for the adsorption/desorption process. A representative Langmuir adsorption isotherm using gravimetric data is given in figure 5.

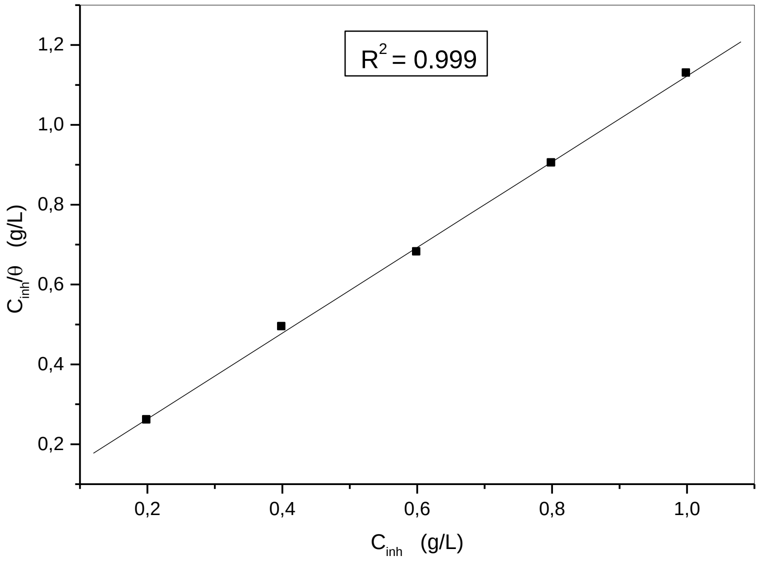

Figure-5: Langmuir adsorption isotherm of ZPAL extract on the C-steel surface in 1M HCl.

These plots are linear with a slope of 1.07, proving that the adsorption of the ZPAL extract from 1M HCl solutions obeys the Langmuir adsorption isotherm. This isotherm assumes that the adsorbed molecules occupy only one site and there is no interaction among the adsorbed inhibitor molecules [31-33]. The value of equilibrium constant, K_{ads} calculated from the reciprocal of the intercept of the isotherm line was found to be 20.63 L g^{-1}. The high value of the adsorption equilibrium constant K_{ads} reflects the good adsorption ability of the ZPAL extract on metal surface. K_{ads} is related to free energy of adsorption (ΔG_{ads}) according to Equation (10) [34, 35]:

$$\Delta G^0{}_{ads} = -RTln(55.5K_{ads}) \qquad (10)$$

where *R* is the universal gas constant and *T* is the absolute temperature. The value 55.5 in the above equation is the concentration of water in solution in mol L^{-1}. It was not possible to calculate this parameter for ZPAL extract since the average molar mass of extract is unknown. Some authors [36-40], in their study on acid corrosion with plant extracts, noted the same limitation.

CONCLUSION

The main conclusions drawn from this study are:

- *Zygophyllum Album L* (ZPAL) extract can be used as an inhibitor of C-steel corrosion in HCl solution.
- The inhibiting effect of ZPAL increases with increase of inhibitor concentration.
- Anodic and cathodic polarization curves indicated that the ZPAL extract is mixed-type inhibitor.

- The adsorption of the ZPAL extract on the C-steel surface was found to obey the Langmuir model isotherm and leads to the formation of a protective film.
- Inhibition efficiency decreased with increasing temperature and their addition led to increase of the activation corrosion energy.
- The Good agreement between the inhibition efficiencies calculated using different techniques (weight loss, EIS, polarization curves,) was obtained.

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