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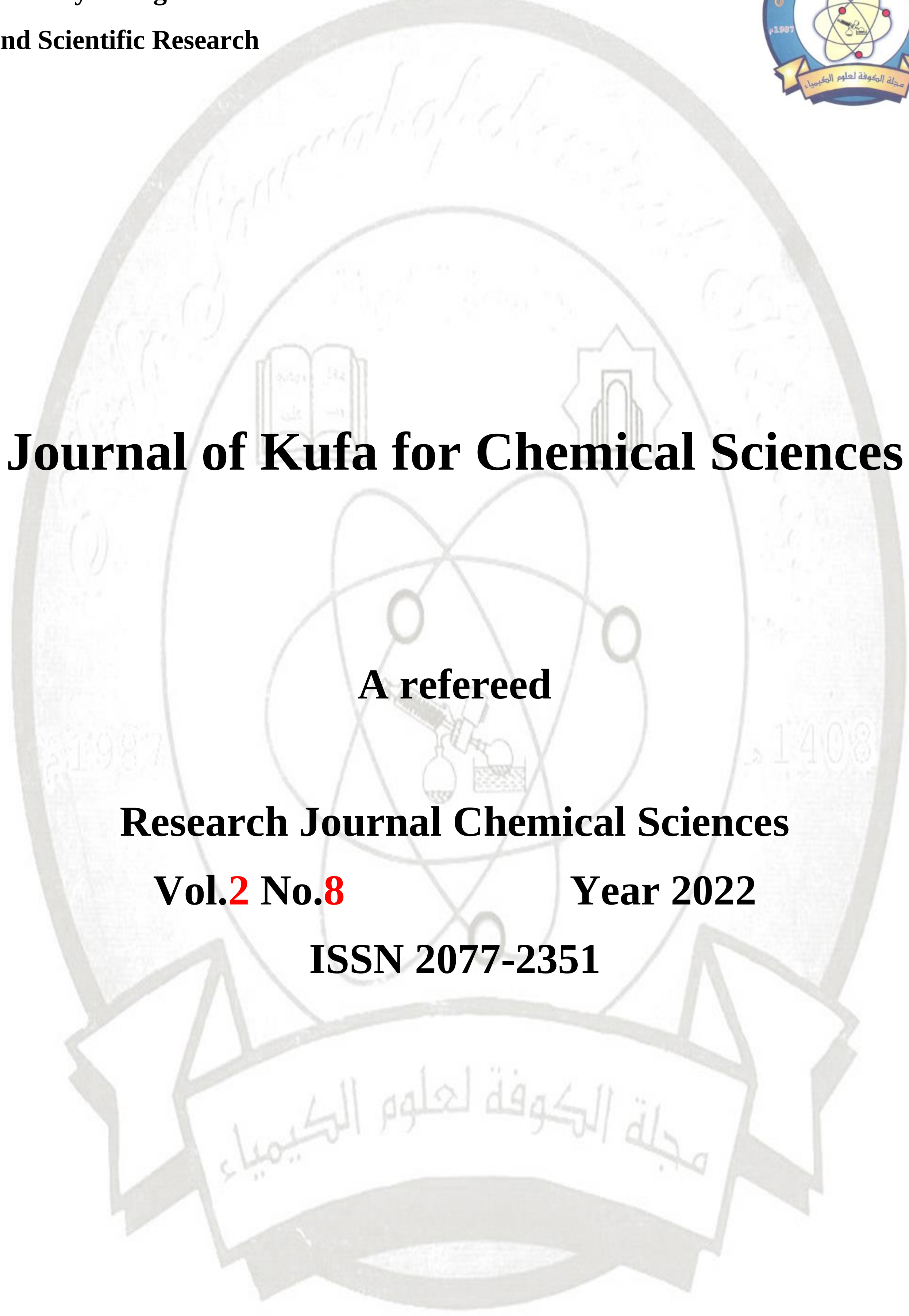

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Evaluation of the Methanolic Extract of *Petroselinum Crispum* (*Parsley*) as Antioxidant and Green Corrosion Inhibitor for Carbon Steel Alloy in Acidic Medium

Sarah Z. Al-Ashoor[1], Dawood S. Ali[2] and Hadi.Z. Al-Sawaad[3]

Chemistry Department, University of Basrah, Iraq. Email:
hadi.ziara@uobasrah.edu.iq.

ABSTRACT

In this study, *Petroselinum Crispum (Parsley*) leaves were extracted by methanol 70% solvent using the maceration extraction method. The extract was examined as a green corrosion inhibitor for carbon steel alloy (C1010) in 0.1 M Hydrochloric acid at different concentrations and temperatures. The extract showed the highest inhibition efficiency of 97.12% at 25℃. The inhibitor's efficiency was reduced when the temperature increased. Kinetic parameters (Ea, ΔH*, and ΔS*) were calculated. The corrosion reaction was repressed by the extract, because the energy barrier of the corrosion reaction was increased, and it became an endothermic process. On the other hand, antioxidant activity was also studied by *in vitro* DPPH assay through different concentrations. Thus, the methanol extract of *Petroselinum Crispum (Parsley)* can be used as a green corrosion inhibitor because it doesn't contain toxic compounds.

KEYWORDS: Parsley, Hydrochloric acid, corrosion, Dpph, Green corrosion inhibitor.

1. INTRODUCTION

Petroselinum crispum Fig.1 belongs to the Apiaceae or Umbelliferae family and the genus *Petroselinum*. *Parsley* was prized for its therapeutic characteristics long before it became accepted as a food or spice. It was most likely originally consumed in Europe during the Middle Ages. Because it helps cleanse the breath and palate, the curly-leafed variety quickly found its way into plates and recipes [1]. Parsley has long been used to cure illnesses such as high blood pressure, allergies, and inflammatory illnesses[2]. It's now frequently used as a dried spice or as a fresh culinary herb. It has a vivid green color and a moderate, bitter flavor that goes well with a variety of dishes. Parsley has a high nutritional content and may have several health benefits [3]. Plants extracts have been used as green corrosion inhibitors in the past and are eco-friendly, nonpoisonous, inexpensive, and significantly available[4]. Corrosion of metals and alloys, certainly in acidic medium, is a significant industrial issue[5]. Corrosion is a naturally occurring phenomenon that ruins a metallic material or its properties as a result of a reaction with its environment, it can damage everything from pipelines constructions, bridges, and public buildings to cars, water, and wastewater systems, and even house implements and is thus one of the most significant issues in the industrial facilities, particularly in the oil and gas industry [6]. Paths available for avoiding corrosion include applications of protective coatings to metal surfaces, adding of chemical species to the environment to prevent corrosion, modifying alloy composition, and treatment of the surface of the metal are all techniques for controlling corrosion. However, recent ways in corrosion research include the production of environmentally acceptable inhibitors and finding techniques to make corrosion useful[7]**.**

Fig 1. *Parsley* herb

2. EXPERIMENTAL

2.1. *Plant material*

Parsley leaves were collected after being bought from the local market, washed well, and dried then, ground to fine powder by the electric mill, and saved in a dry bottle at 25℃.

2.2. *Parsley methanolic extract preparation*

Parsley extract was prepared by the maceration method[8]. (25) gram of *Parsley* leaves powder was prepared by maceration procedure using Methanol (70%) as a solvent (200 mL) for 72h at room temperature with occasional stirring. After the maceration, extracts were collected, filtered using Whatman's No.41 filter paper, and evaporated to dryness under a rotary evaporator at 40℃ to obtain the *Parsley* methanol crude extract. The crude extract was kept in dark glass bottles at 4℃ until used for further analysis.

2.3. *Phytochemicals Screening*

Chemical tests were carried out on the methanol extract by using the typical procedure to identify the constituents of the extract, by characteristic color changes as described by[9-13]

2.4. *Antioxidant activity*

2.4.1. *Preparation of DPPH solution*

DPPH (1,1-diphenyl-2-picrylhydrazyl) solution (0.04 mg/mL). In a measuring flask, 2 mg (0.002g) of DPPH was weighed and dissolved in 50 mL of methanol.

Preparation of sample solutions

A stock solution of 1000 µg/mL of *parsley* leaves extract was prepared, i.e., 10 mg in 10 mL methanol. It was also diluted in a series of concentrations of (100, 250, 500, 750) µg/mL using a methanol solvent.

2.4.2. *Measurement of antioxidant capacity*

The blank antioxidant capacity was determined by mixing 2 mL DPPH with 3 mL methanol then incubating at 25°C for 30 minutes. At 517 nm, the absorbance of each solution was measured. The antioxidant capacity of a methanol extract of *parsley* leaves was measured quantitatively by piping 1 mL of extract solution at various concentrations, followed by 2 mL of DPPH and 2 mL of methanol, respectively. They were incubated at 25°C for 30 minutes before being measured at the same wavelength (517 nm). If the color changes from purple to pale yellow, that will indicate the presence of antioxidant inhibition of the extract[10].

2.5. *Corrosion Study*

2.5.1. *Preparation of working electrodes*

Carbon steel alloy strips with the following dimensions were used: 5 cm in length, 1 cm in breadth, and 0.1 cm in thickness. The strips had a total area of 11.1 cm2, and they were ground to various smoothness (80, 120, 200, 400, 600) with different grades of Silicon carbide paper. The specimens were then washed well with distilled water and ethanol and then dried with hot air. During the time between polishing and polarization measurements, the specimens were kept in a desiccator containing silica gel[11].

2.5.2. *Alloy composition*

The elements of the carbon steel (C1010) alloy used in this study are illustrated in Table 1.

Table 1. Carbon steel (C1010) alloy chemical composition

C%	*Mn%*	*P%*	*S%*	*Cu%*	*Si%*	*Cr%*	*As%*	*Ni%*	*Fe%*
0.13	0.30	0.05	0.04	0.30	0.37	0.10	0.08	0.30	Balance

2.5.3. *Electrochemical Cells*

The electrochemical cell used in this experiment consists of a 100 mL beaker with three electrodes: a platinum electrode (Auxiliary electrode), a carbon steel specimen as the working electrode, and a saturated calomel electrode (SCE) as a reference electrode.

2.5.4. *Potentiodynamic studies (Tafel plots)*

This technique is commonly engaged for measuring corrosion resistance and a wide variety of functions, to measure current density *vs*. electric potential, through setting up the open circuit potential (OCP) for 20 minutes. The polarization curve can be acquired by scanning in the potential range between –250 to +250 mV (*vs*. OCP) using a computer to control a potentiostat/galvanostat at a scanning rate of 10 mV s^{-1}.

2.5.6. *Preparation of solutions*

The methanolic extract was individually made at various concentrations (1, 2, 8, and 9) ppm by using HCl acid as a corrosive environment at 298 K and the optimal concentration was studied then at different temperatures (308, 318, and 328 K) in presence of HCl as the corrosive medium.

RESULTS

Phytochemicals Screening

Phytochemical screening for methanol extract of *parsley* revealed that, the presence of flavonoids, phenols, carbohydrates, Tannins, saponins, Alkaloids, fixed oils, and fats as summarized in Table 2.

Table 2. Phytochemical screening of methanol extract of *Parsley*

Phytochemical	**Flavonoids**	**Phenols**	**Saponins**	**Alkaloids**	**Carbohydrates**	**Tannins**	**Fixed oils and fats**
Parsley methanol extract	+++ (Alkaline Reagent)	+++ (5% $FeCl_3$)	+++ (Foam test)	++ (Wagner's reagent)	++ (Molish test)	++ (10% $FeCl_3$)	++ (Stain test)

The Phytochemical analysis of the methanol extract as in Table 2 above depicts that the methanol extract gives a positive detection with all phytochemicals that be tested.

Antioxidant activity

Table 3 below showed the results of scavenging activity on DPPH of *parsley* methanol extract with IC_{50} value.

Table 3 Scavenging activity of the *parsley* methanol extract on DPPH

Extract	***Concentrations (µg/mL)***	***Scavenging activity %***	
		Methanol extract	***Gallic acid***
***Parsley* methanol extract**	**100**	**58.59**	**51.84**
	250	**70.07**	**62.59**
	500	**70.87**	**79.66**
	750	**73.12**	**91.57**
	1000	**78.92**	**96.83**
	IC_{50}(µg/mL)	**32.48**	**2.16**

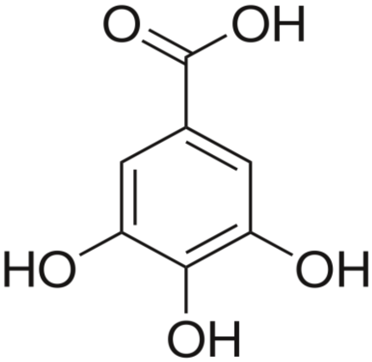

Fig 2. Gallic acid structure

Free radicals are usually used as a model in measuring an antioxidant activity with absorbance values at 517 nm[12]. The DPPH free radical reduction method, which is based on the reduction of a solution of colored DPPH free radicals by the inhibition of the free radicals, is used to determine antioxidant activity. The DPPH will be reduced when the purple DPPH solution comes into contact with the electron donor material, and the purple colour will be replaced with yellow from the picryl group.[13].

The IC_{50} value, which is the concentration of the sample solution necessary to inhibit 50% of DPPH free radicals, indicates the number of antioxidant activities. The IC_{50} value came out to be 32.48 µg/mL. If the IC_{50} value is less than 100 µg/mL, the antioxidant activity is said to be strong (µg/mL) that can inhibit 50% of oxidation. The calculation of the effective concentration value or IC_{50} stated that the antioxidant activity of *Parsley* leaves was strong. The positive control gallic acid Fig.2 showed a higher IC_{50} (2.16 µg/ml). Fig.3 and Fig. 4 show the scavenging activity of the methanol extract and color-changing from violet to yellow that indicating the presence of antioxidant activity respectively.

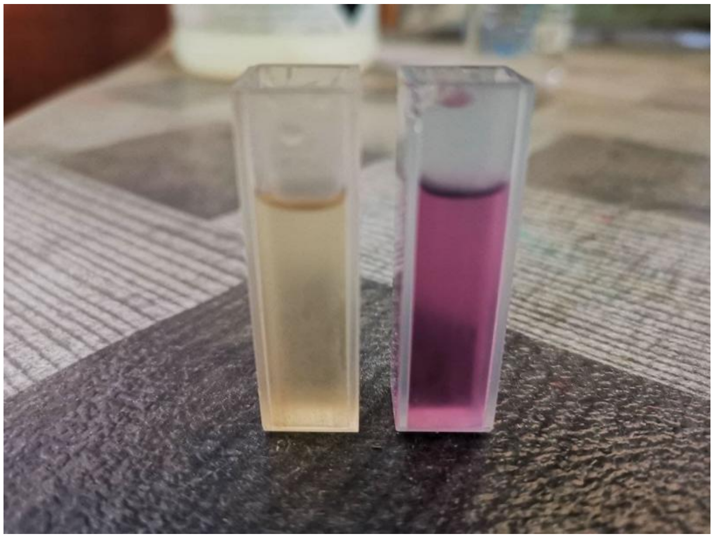

Fig 3. Color changing of the extract from violet to yellow.

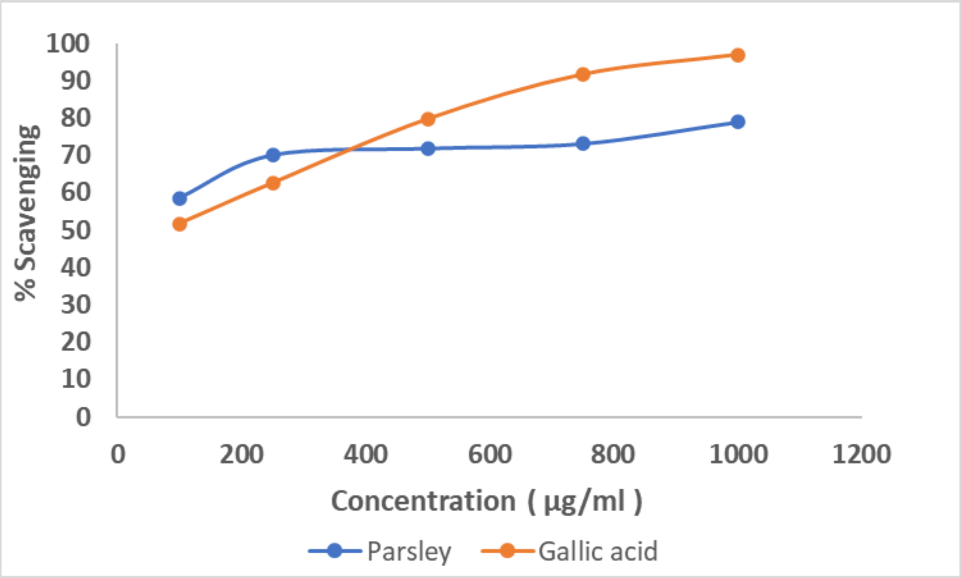

Fig 4. Scavenging activity of the extract and the positive control

Corrosion study

The methanol extract of *Parsley*. was examined as a green corrosion inhibitor for the carbon steel alloy against (0.1 M HCl acid) as the corrosive environment. The electrochemical data for carbon steel alloy surface in the presence of different concentrations of methanol extract compared with the blank were obtained by plotting the Tafel plots for these cases as in Figure 5 below and the data were summarized in Table 4 below at 25 ˚C.

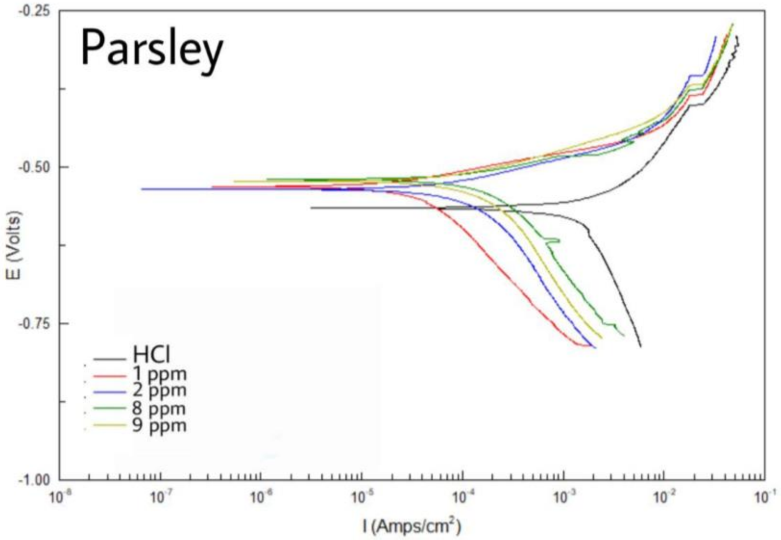

Fig.5 Tafel plots for carbon steel alloy in presence of a different concentration of methanol extract of *Parsley* compared with the blank at 25℃.

Table 4. The Electrochemical data for the corrosion of carbon steel alloy surface in presence of different concentrations of methanol extract of *Parsley* relative to blank at 25 ˚C.

Conc (ppm)	Ecorr (mV)	I_{corr} (µA.cm^{-2})	CR (mpy)	βa (mV/de)	βc (mV/de)	R_p (Ω.cm^2)	%IE	θ
(3650) for Blank	**- 567**	**1569.2**	**726.65**	**213.23**	**- 198.36**	**11.471**	–	–
1	**- 533**	**45.038**	**20.856**	**46.525**	**- 114.64**	**399.66**	**97.12**	**0.9712**
2	**- 537**	**108.25**	**50.127**	**68.784**	**- 255.41**	**1662.9**	**93.10**	**0.9310**
8	**- 521**	**192.12**	**88.967**	**72.204**	**- 278.51**	**936.91**	**87.75**	**0.8775**
9	**- 524**	**132.08**	**61.164**	**69.629**	**- 251.33**	**1362.8**	**91.58**	**0.9158**

Table.4 above showed the electrochemical data obtained from Tafel plots at several concentrations of the methanol extract of *parsley* as anti-corrosion agents for carbon steel alloy in HCl corrosive medium. As in Table 4 above, the *parsley* extract optimal concentration is 1 ppm with inhibition efficiency (97.12)% where, if the concentration of extract is raised, the efficiency is reduced, this can be attributed to less compatibility between the extract (inhibitor) with the alloy's surface as concentration increased[14]. In general, the resistance polarization Rp for the surface of the studied alloy was increased in the presence of any concentration of the inhibitor compared with the absence that leads to reduction in corrosion current density I_{corr} and corrosion rate (CR). The Tafel constant values (β_a and β_c) as in Table 4 are irregularly reduced for anodic values while they are raised for cathodic values as the concentration of the inhibitor increased, this case can be assigned to the behavior of the inhibitor has the ability to hydrogen evolution mechanism controlled with the simple blocked reaction for the anodic site. [15], [16]. On the other hand, E_{corr} values depicted that the behavior of the inhibitor is mixed[17]

Furthermore, when the temperature was raised from 25˚C to 55 ˚C, the I_{corr} and CR values raised and Rp was reduced this is because to increasing of the kinetic energy for the corrosive environment molecules to attack toward the surface of alloy where the dissolution of the anode (alloy's steel) and hydrogen evolution (reduction for the corrosive acid) occurred[18]. The data is summarized in Table 5 below.

Table 5. Corrosion rates of the corrosive environment at different temperatures

Temp (K)	Error (mV)	I_{corr} (μA.cm^2)	CR (mpy)	βa (mV/de)	βc (mV/de)	R_p (Ω.cm^2)
298	**- 567**	**1596.2**	**726.65**	**213.23**	**-119.36**	**11.471**
308	**- 563**	**1740.06**	**806.05**	**283.06**	**-117.14**	**10.341**
318	**- 571**	**1891.12**	**875.75**	**131.53**	**-121.3**	**9.581**
328	**- 549**	**2734.2**	**1266.1**	**465.17**	**-111.03**	**6.533**

On the other hand, in the presence of the inhibitor, when the temperature was raised from 25˚C to 55 ˚C, as in Table 6 below that acquired from Fig.6 below, the inhibitor efficiency and R_p are reduced due to the reducing of the surface coverage area film, but increasing in I_{corr} and CR because the surface of alloy can be attacked by the corrosive molecules easily [19], [20].

Table 6. The Electrochemical data for the corrosion of carbon steel Alloy surface in the presence of different concentrations of methanol extract relative to blank at different temperatures

Temp (K)	**E_{corr} (mV)**	**I_{corr} (μA.cm^2)**	**CR (mpy)**	**βa (mV/de)**	**βc (mV/de)**	**R_p (Ω.cm^2)**	**%IE**	**θ**
298	**- 533**	**45.038**	**20.856**	**46.525**	**114.64**	**399.66**	**97.12**	**0.9712**
308	**- 531**	**483.77**	**224.02**	**116.15**	**531.19**	**37.208**	**72.19**	**0.7219**
318	**- 526**	**1141.9**	**528.77**	**275.94**	**2255.5**	**15.764**	**39.61**	**0.3961**
328	**- 537**	**2339.1**	**1083**	**276.57**	**2125.5**	**7.695**	**14.45**	**0.1445**

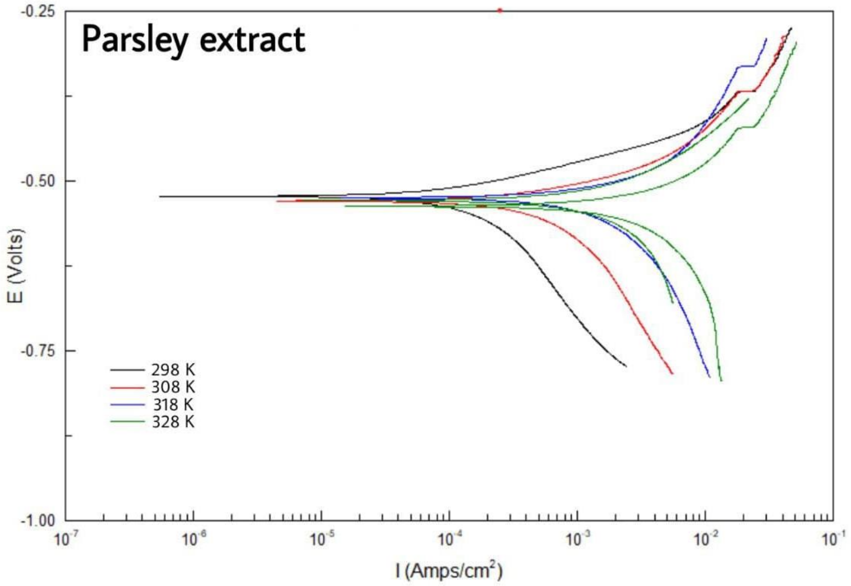

Fig 6. Tafel plots for five concentrations of methanol extract compared with a blank at different temperatures.

To understand more on the behavior of the corrosion reaction in the absence and the presence of the inhibitor, kinetic parameter like activation energy E_a^* for the corrosion reaction of iron alloy in the absence and the presence of inhibitor was calculated according to Arrhenius equation [21] as in below:

$$\ln(CR) = \ln A - \frac{E_a^*}{RT} \qquad (1)$$

Where, E_a^* is an activation energy for corrosion reaction (kJ.mol^{-1}), A is Arrhenius factor (s^{-1}), T is an absolute temperature (K) and R is the universal gas constant ($8.314\ J.K^{-1}.mol^{-1}$). By plotting the above relationship i.e., ln (CR) against (1/T), E_a^* is calculated as in Fig.7 and 8 below:

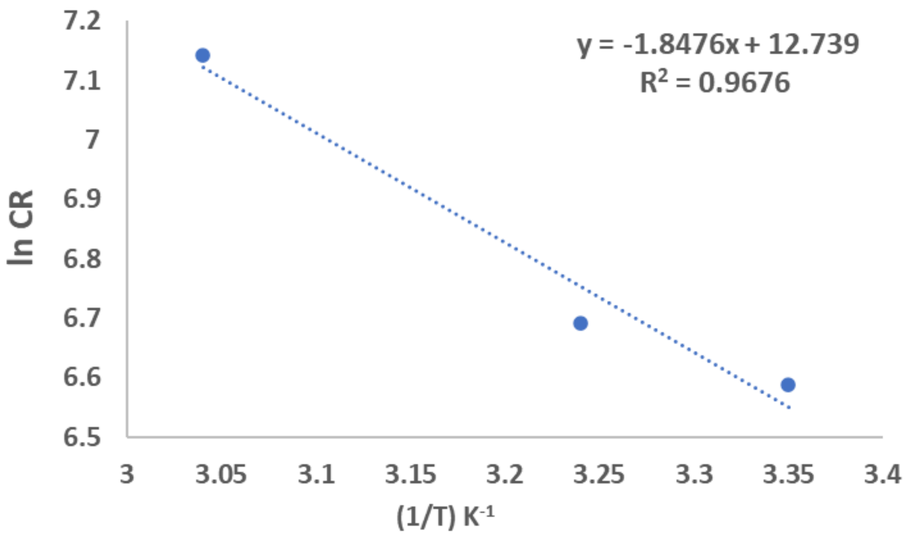

Fig 7. Calculation of activation energy for the corrosion reaction of carbon steel alloy in the absence of the inhibitor.

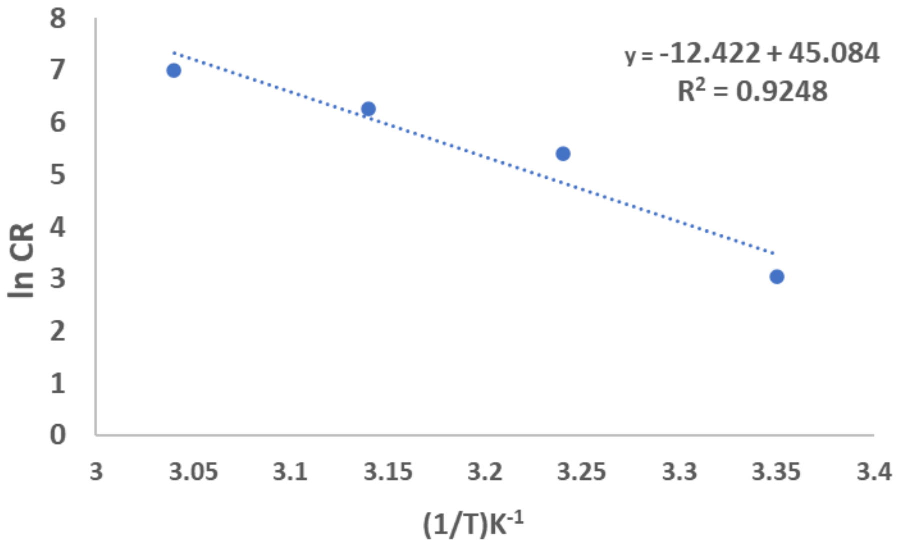

Fig 8. Calculation of activation energy for the corrosion reaction of carbon steel alloy in presence of the inhibitor.

On the other hand, other kinetic parameters like enthalpy of activation ΔH^*, entropy of activation ΔS^*, were calculated where and were calculated according to the following equation [15], [20].

$$\ln\left(\frac{CR}{T}\right) = [\ln(\frac{R}{Nh}) + \frac{\Delta S^*}{R}] - \frac{\Delta H^*}{RT} \qquad (2)$$

Where, N is Avogadro's number $(6.023 \times 10^{23} mol^{-1})$ and the Plank's constant which is equal to $(6.625 \times 10^{-34} J.s)$, by plotting of $\ln\left(\frac{CR}{T}\right)$ against, the slope is equal to $\frac{-\Delta H^{*}}{R}$ and the intercept equal to $\ln[(\frac{R}{Nh}) + \frac{\Delta S^{*}}{R}]$ as in Fig.9 and 10 below:

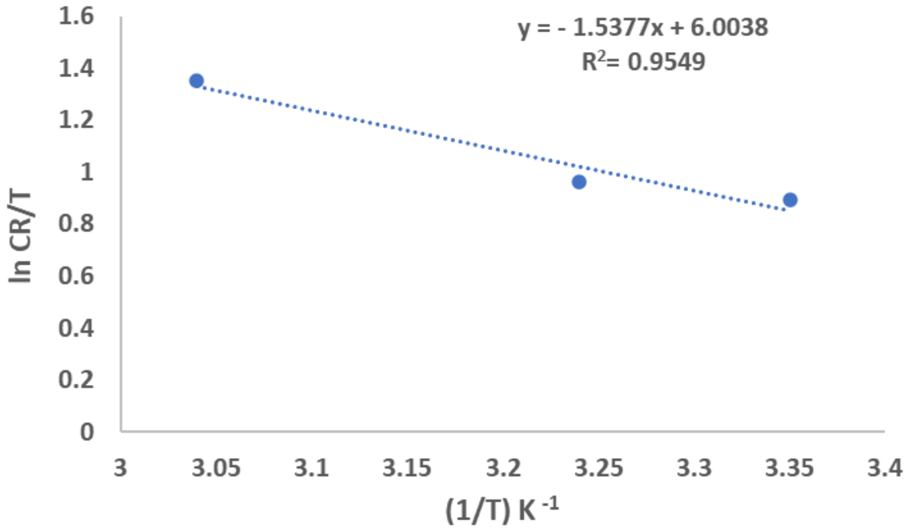

Fig 9. Calculation of the enthalpy and entropy of activation for the carbon steel alloy in the absence of the inhibitor.

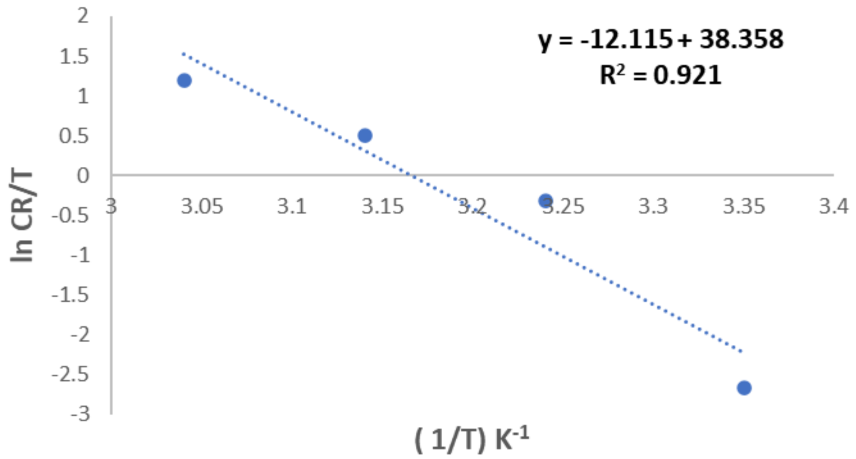

Fig 10. Calculation of the enthalpy and entropy of activation for the carbon steel alloy in the presence of the inhibitor

Thus, data of kinetic parameters can be summarized in Table 7. Below:

Table 7. Kinetic parameters for the corrosion reaction of the carbon steel alloy in the absence and presence of inhibitor at optimal concentration.

Comp.	*Conc.*	E_a^* $(kJ.mol^{-1})$	A (s^{-1})	ΔH^* $(kJ.mol^{-1})$	ΔS^* $(J.K^{-1}.mol^{-1})$
HCl	-------	15.36	$3.4078\ x10^{5}$	12.78	-91.62
Methanol extract	1 ppm	114.6833	4.5568×10^{16}	355.6	158.0665

It is thus concluded that chemical adsorption of the inhibitor occurs, this increase in *E*a value in the presence of the inhibitor compared with the absence is attributed to an significant decrease in the adsorption process of corrosive molecules (HCl molecules) on the alloy surface [22].

The corresponding increasing in the corrosion rate is also attributed to the greatest area of the metal exposed to the corrosive environment (acidic medium), namely, HCl, The positive sign of ΔH^* refers to the endothermic nature of the dissolution process whether in the absence or presence of the inhibitor which implies that the dissolution of the alloy is increased as temperature increased but it becomes difficult in the presence of inhibitors, the enthalpy of activation value in presence of the inhibitor as in Table 7 reveals the adsorption of the inhibitor is chemical because this value is greater than 100 $kJ.mol^{-1}$ [22-23]

The Arrhenius factor depicted that the vibration of the corrosive molecules is increased in the presence of the inhibitor because the ferric oxide molecules tend to restrict the inhibitor molecules to form a stable adsorbed film on the surface film [25]. The entropy of activation in the absence of the inhibitor is negative while in the presence of inhibitor is positive these two cases can be interpreted due to the corrosive molecules in the absence of the inhibiter arranged themselves on the alloy's surface while, in the presence of the inhibitor the corrosive molecules moved towards the inhibitor molecules to form an activated complex as the slow rate-determining step to make a stable adsorbed film on the surface alloy[22]

CONCLUSION

Several points can be summarized below as conclusions:

1- Methanolic extract of Parsley is an excellent corrosion inhibitor for the carbon steel alloy at a corrosive environment (0.1 M HCl). The extract showed high inhibition efficiency (97.12%), with optimal concentrations (1 ppm), at 25 ºC.

2- The efficiency of the inhibitor decreases with increasing of the temperature.

3- The behavior of the inhibitor is mixed and chemical adsorbed.

4- Parsley methanolic extract shows high antioxidant activity (IC50 = 32.48 µg/ml).

5- The inhibitor contributes to increase activation energy E_a^* of the carbon steel alloy corrosion reaction and the inhibitor also behaves as a mixed inhibitor.

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