



Green Corrosion Inhibitors for Carbon Steel by Green Leafy Vegetables Extracts in 1 M HCl

GHADAH M. AL-SENANI, SAMEERAH I. AL-SAEEDI and RASMIAH ALMUFARIJ

Department of Chemistry, College of Science, Princess Nourah
Bint Abdulrahman University, Riyadh, Saudi Arabia.

*Corresponding author E-mail: gmalsnany@pnu.edu.sa

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ABSTRACT

The effect of some Green Leafy Vegetables (*GLV*) extracts namely *Lactuca sativa* (*Lactuca*), *Eruca Sativa* (*Arugula*), *Petroselinum crispum* (*Parsley*), and *Anethum Graveolens* (*Dill*) were investigated on inhibition of corrosion carbon steel in 1 M HCl solution using gravimetric (weight loss) method. The inhibition efficiency has increased as concentration of the extract increased. The inhibition efficiency has decreased as the temperature increased. The results obtained showed that *GLV* extracts inhibited the corrosion process by a physical adsorption mechanism that followed the Langmuir, Freundlich, and Temkin adsorption isotherm models. The adsorption thermodynamic parameters that were calculated include, free energy of adsorption (ΔG_{ads}°), activation energy (E_a), enthalpy of adsorption (ΔH_{ads}°), and entropy of adsorption (ΔS_{ads}°) are proposed for the corrosion of carbon steel in 1 M HCl in the absence and presence of *GLV* extract.

Key words: Carbon steel, Hydrochloric acid, Corrosion inhibition, Green Leafy Vegetables, Adsorption.

INTRODUCTION

Carbon steel is widely used in industries due to its good mechanical properties carbon steel it has been extensively used under different conditions in chemical and allied industries in presence of alkaline, acid and salt solutions. The investigation of corrosion of carbon steel is always a subject of high theoretical as well as practical interest. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and

accelerate corrosion. One way of protecting steel from corrosion is to use corrosion inhibitors. The known dangerous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitors for several metals in different media.

Recently, plant extracts have again become important as an environmentally acceptable, readily available, and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of natural chemical compounds that can be extracted by simple procedures with low-cost, and so the study of using plant extracts as corrosion inhibitors is an important scientific research field due to both economic and environmental benefits¹.

There are several reviews on the use of plant extracts as corrosion inhibitors. Recently aqueous extract of Banana peel². The inhibitive action of Fruit peel aqueous extract³, eco-friendly inhibitor L-Valine-Zn²⁺⁴, Eucalyptus Camaldulensis leaves extract⁵, Ethanol extract of Fagus Sylvatica leaves⁶, Gnetum Africana leaves extract⁷, Osmanthus Fragran leaves extract⁸, Seed extract of Psidium guajava⁹, aqueous extract of Propolis¹⁰, Juniper Oxycedrus extract¹¹, Anemone Coronaria extract¹², aqueous Garlic peel extract¹³, Garlic extract¹⁴, Fennel (Foeniculum Vulgare)¹⁵, extract of Limonium Thouinii (Plumbaginaceae)¹⁶, modified Cassava Starches¹⁷, carboxy methylated Cassava Starch¹⁸, Sesbania Sesban Extract¹⁹, Rosemary extract²⁰, UAE Neem extract²¹. *Murraya koenigii* (curry leaves) extract²², *Chenopodium Ambrorsioides* extract²³, *Asteriscus Imbricatus* extracts²⁴ and Argan Press Cake extract²⁵ have been investigated.

On the other hand, there are no studies on the use of green leafy vegetables (GLV) as inhibitors for carbon steel in acidic solutions has been published as far as use know.

MATERIALS AND METHODS

Specimen preparation

Tests were performed on carbon steel specimens with the following composition (in wt. %) C 0.42%, Mn 1.23%, Si 0.265%, S 0.004%, P 0.011%, Cr 0.008%, Cu 0.024%, Sa 0.0016%, Ni 0.0214%, Ti 0.017%, Al 0.035%, Nb 0.036%, Ca 0.002% and Fe balance. Carbon steel circular strips of the same composition with an exposed area of 1 cm² were used. Before each test, the specimen were ground with 800 and 1200 grit grinding papers, and then cleaned by distilled water and acetone.

Preparation of plant extract

GLV were dried in an electric furnace for 10-20 min then ground to powder. GLV dried powder (5g) were mixed with 500 ml of 1 M HCl and refluxed at 50°C for 2 h. The extracts were cooled, and filtered through Whatman filter paper. The filtrate was then kept as the stock solution. Working solutions of different concentrations ranging from 20 to 60 % (v/v) were prepared from the stock solutions by dilution with 1 M HCl solution.

Fourier transform infrared spectroscopy (FT-IR)

A KBr pellet was made from the dried extracts and were characterized using FT-IR (Nicolet's auxiliary experiment module - AEM, Omnic software).

Gravimetric (weight loss) method

In the gravimetric experiment, a previously weighed carbon steel specimens was completely immersed in 100 mL of 1 M HCl solution with and without the inhibitor for a period of 3 h. Then, the specimens were washed, dried and weighed. The weight loss was calculated. The experiments were repeated at different concentrations (20 - 60%), different temperatures (25°C – 60°C), and different times of immersion (3 – 15 h). From the weight loss results, corrosion rates (C.R), degree of surface coverage (θ), and the inhibition efficiency (E_{inh} %) of the inhibitor were calculated using Eq. (1)–(3), respectively²⁵ and displayed in Table 1:

$$C.R = \frac{W}{At} \quad \dots(1)$$

$$\theta = \frac{W_o - W_{inh}}{W_o} \quad \dots(2)$$

$$E_{inh} \% = \frac{W_o - W_{inh}}{W_o} \times 100 \quad \dots(3)$$

where A is the area of the carbon steel specimens (in cm²), t is the immersion time (in hours) and W is the weight loss of carbon steel after time, t, W_o and W_{inh} are the weight losses (mg) for carbon steel.

RESULTS AND DISCUSSION

aromatic ring, which commonly gather in corrosion inhibitors.

FTIR results of GLV extracts

The important IR absorption bands of inhibitors are given in Fig. 1 and their respective FT-IR peaks are given in Table 1. These results showed that the inhibitors containing functional groups with O and N atoms and other attached to

Effect of GLV Concentration

The results indicate that the corrosion rate of carbon steel has decreased with increasing inhibitors concentration. The values of corrosion rates (C.R), and the inhibition efficiency (E_{inh} %)

Table 1 : FT-IR peaks of GLV extracts

Inhibitors	Peaks from FT-IR spectra	Possible functional groups
(A) Lactuca sativa(Lactuca)	414.78	C-C (aliphatic)
	603.00	-C=C stretch
	1055.94	PO-C stretch
	1245.22	OSO ₂ -O
	1407.43	XSO ₂ -X
	1614.37	C=N stretch
	2922.57	C-H (aromatic)
	3345.47	NH ₂ stretch
	3738.73	N-C (aromatic)
	(B) Eruca sativa(Arugula)	403.55
604.99		-C=C stretch
1065.91		PO-C stretch
1247.01		OSO ₂ -O
1414.56		XSO ₂ -X
1623.94		C=N stretch
2923.70		C-H (aromatic)
3342.25		N-H stretch
(C) Petroselinum crispum(Parsley)		403.20
	617.89	-C=C stretch
	1068.10	PO-C stretch
	1247.46	OSO ₂ -O
	1411.10	XSO ₂ -X
	1614.22	C=N stretch
	2927.20	C-H (aromatic)
	3339.39	N-H stretch
(D) Anethum graveolens(Dill)	410.82	C-C (aliphatic)
	606.26	-C=C stretch
	1056.64	PO-C stretch
	1407.95	XSO ₂ -X
	1615.04	C=N stretch
	2922.35	C-H (aromatic)
	3348.16	N-H stretch
	3730.07	N-C (aromatic)

obtained from the weight loss for different inhibitors concentrations at room temperature in 1 M HCl are given in Table 2. From the values obtained, it is obvious that there is a decrease in the corrosion rate of carbon steel proportional with an increase in the concentration of GLV. This indicates that the GLV in the solution inhibits the corrosion of carbon steel in HCl and that the extent of corrosion inhibition depends on the amount of GLV present. From Fig. 2, it is clear that inhibition efficiency increased with increasing the inhibitors concentration. The maximum value of inhibition efficiency (E_{inh} %) obtained for 50% of (C) *Petroselinum crispum* (Parsley) is 81.39%, and the efficiency of inhibitor remained constant at concentration 60%. Due to the complex compounds or high phytochemical constituents of *Petroselinum crispum* (Parsley), it is difficult to assign the inhibiting action to a particular constituent or group of constituents. The inhibitor

molecules present in the extracts block the surface of carbon steel via adsorption mechanism²⁶.

Effect of Immersion Time

The effect of immersion time on the weight loss of carbon steel in 1 M HCl and in the presence of 50% of GLV extracts were studied at 25°C. As shown in Fig. 3, it is found that weight loss of carbon steel varies with time in HCl, and was reduced in the presence of the extracts compared to the blank. The decrease in weight loss in the presence of inhibitors may be due to the adsorption of the phytochemical constituents on the surface of the carbon steel in the extract²⁷.

Effect of Temperature

The effect of temperature on the inhibition efficiency of carbon steel in 1 M HCl and in the presence of 50% of GLV extracts were studied at

Table 2: The values of C.R, and E_{inh} % for different inhibitors concentrations at 25°C in 1 M HCl

Inhibitors GLV	Concentration (v/v)%	Corrosion Rates (C.R mg/cm ² .h)	Inhibition Efficiency (E_{inh} %)
Blank	0	1.86	-
(A) Lactuca sativa (Lactuca)	20	0.90	51.59
	30	0.70	62.27
	40	0.69	63.05
	50	0.56	69.72
	60	0.43	76.71
(B) Eruca Sativa (Arugula)	20	0.90	51.60
	30	0.72	61.53
	40	0.51	72.81
	50	0.44	76.39
	60	0.36	80.83
(C) Petroselinum crispum (Parsley)	20	0.55	70.22
	30	0.54	71.15
	40	0.52	72.08
	50	0.35	81.39
	60	0.35	81.39
(D) Anethum Graveolens (Dill)	20	0.90	51.48
	30	0.83	55.53
	40	0.78	58.22
	50	0.72	61.57
	60	0.67	63.93

various temperatures (25 - 60°C) during 3 h of immersion. Fig. 4 show evolution of weight loss with absence and presence of the 50% GLV at different temperatures, and indicates that at 50% GLV, the weight loss of carbon steel has increased with temperature increase. It shows as well that inhibition efficiency has decreased at higher temperatures (Fig. 5). This is due to the increased rate of dissolution of carbon steel and partial desorption of the inhibitor from the metal surface with temperature^{28,29}. On other hand, the decrease in inhibition efficiency with increasing in temperatures reveals physical adsorption mechanism (physisorption) and may be due to increase in solubility of the protective film formed rapidly on carbon steel surface, which is believed to inhibit the process of corrosion²⁷.

Adsorption Isotherms and thermodynamic parameters

The mode and extent of the interaction between the GLV inhibitors and the carbon steel surfaces were studied by applying adsorption isotherms. The Langmuir, Freundlich, and Temkin approach were used to determine the adsorption mechanisms of the inhibition reaction, the isotherms were best described by the adsorption behavior of the GLV extracts on the surface of carbon steel.

Langmuir adsorption isotherm can be expressed according to Eq. 4³⁰⁻³²:

$$\theta = \frac{K_{ads} C_{inh}}{1 + K_{ads} C_{inh}} \quad \dots(4)$$

Table 3: Langmuir, Freundlich and Temkin adsorption isotherm parameters for adsorption of GLV extract on the surface of the carbon steel

Isotherm	Inhibitors GLV	Slope	Intercept	R ²	K _{ads}	-ΔG _{ads} ^o (KJ/mol)
Langmuir	(A)Lactuca sativa (Lactuca)	0.922	21.107	0.985	0.047	2.396
	(B)Eruca sativa (Arugula)	0.876	21.373	0.995	0.047	2.365
	(C)Petroselinum crispum (Parsley)	0.977	12.966	0.996	0.077	3.602
	(D)Anethum graveolens (Dill)	1.372	12.457	0.998	0.080	3.702
Freundlich	(A)Lactuca sativa (Lactuca)	0.385	-1.806	0.984	0.164	5.476
	(B)Eruca sativa (Arugula)	0.418	-1.903	0.981	0.149	5.236
	(C)Petroselinum crispum (Parsley)	0.287	-1.352	0.951	0.259	6.604
	(D)Anethum graveolens (Dill)	0.197	-1.256	0.996	0.285	6.839
Temkin	(A)Lactuca sativa (Lactuca)	0.249	-0.231	0.975	0.396	7.653
	(B)Eruca sativa (Arugula)	0.273	-0.301	0.987	0.332	7.219
	(C)Petroselinum crispum (Parsley)	0.203	0.003	0.962	1.015	9.988
	(D)Anethum graveolens (Dill)	0.113	0.174	0.991	4.664	13.766

Table 4: Thermodynamic activation parameters of carbon steel in 1 M HCl at absence and presence of 50% GLV extract

Medium	Blank	(A)Lactuca sativa (Lactuca)	(B)Eruca sativa (Arugula)	(C)Petroselinum crispum (Parsley)	(D)Anethum graveolens (Dill)
E _{ads} (KJ)	60.867	77.171	73.403	88.270	69.998
ΔH _{ads} ^o (KJ/mol)	58.253	74.557	70.790	85.651	67.384
ΔS _{ads} ^o (KJ/mol K)	-44.312	-1.088	-14.598	33.282	-22.180

where C_{inh} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant. Rearranging this Eq. 4 gives Eq. 5:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad \dots(5)$$

The linear variation of C_{inh}/θ vs. C_{inh} of the GLV in 1 M HCl solutions showed that the adsorption is well fitted by the Langmuir adsorption isotherm (Fig. 6 (a)), the slope and R^2 presented in Table 3. The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient (the degree of fit between the experimental data and the isotherm equation) at different exposure time. The R^2 values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm.

Freundlich adsorption isotherm is given by Eq. 6³³:

$$\theta = K_{ads} C_{inh}^{1/n} \quad \dots(6)$$

and the linearized version by Eqn. (7):

$$\ln \theta = \ln K_{ads} + \frac{1}{n} \ln C_{inh} \quad \dots(7)$$

where n is the measure adsorption intensity. Values of $\ln \theta$ are plotted against $\ln C_{inh}$ (Fig. 6 (b)). The slope and R^2 data are presented in Table 3. From the slope of the Freundlich plot, $1/n$ is above 1, which indicates that it is cooperative adsorption.

Temkin adsorption isotherm assumes a uniform distribution of adsorption energy that increases with the increase in the surface coverage. This is given by Eq. 8^{33, 34}:

$$\theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C_{inh} \quad \dots(8)$$

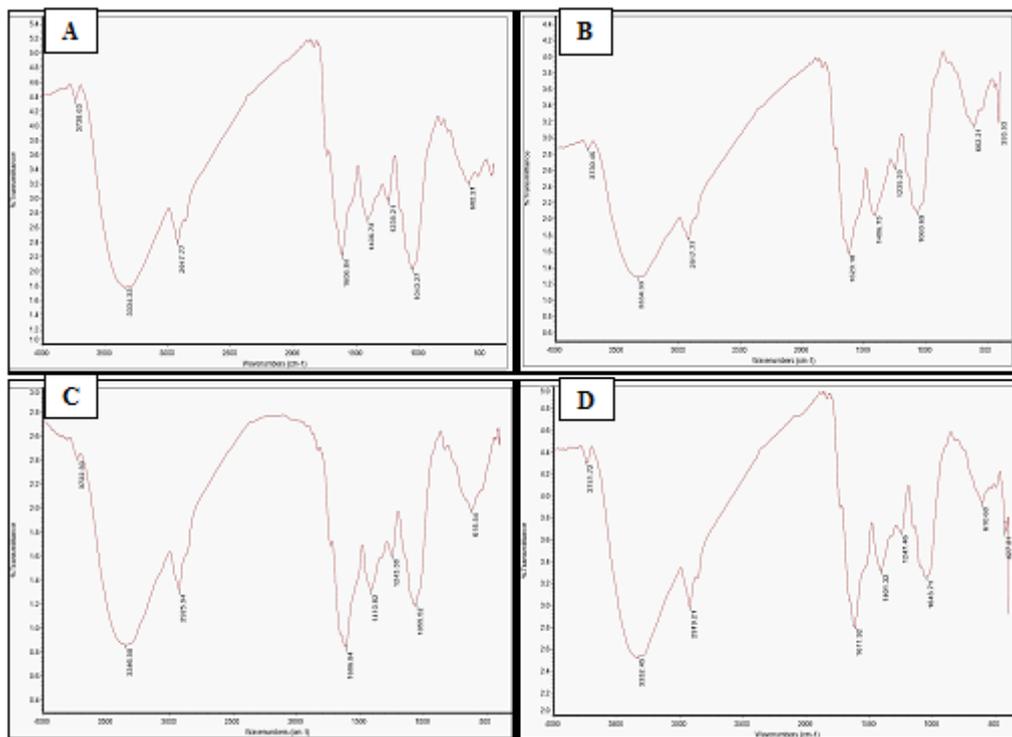


Fig. 1: FTIR spectra of GLV extracts

where f determines the adsorbent-adsorbates interaction. However, the plot of surface coverage θ against the natural logarithm of the concentration of the extract, $\ln C_{inh}$, is shown in Fig. 6 (c), the slope and R^2 are presented in Table 3.

From the Langumir, Freundlich and Temkin isotherms in Table 3, the degrees of linearity R^2 were also close to unity indicating that the *GLV* extracts were strongly adsorbed of on the surface of the carbon steel.

From the intercept of straight lines, K_{ads} values can be obtained and related to the free energy of adsorption, ΔG_{ads}° by Eq. 9 [35]:

$$\Delta G_{ads}^\circ = -RT \ln(55.5K_{ads}) \quad \dots(9)$$

where R is the universal gas constant, T is the absolute temperature and 55.5 is the molar heat of adsorption of water. Results obtained indicate that the values of ΔG_{ads}° are negative in all cases,

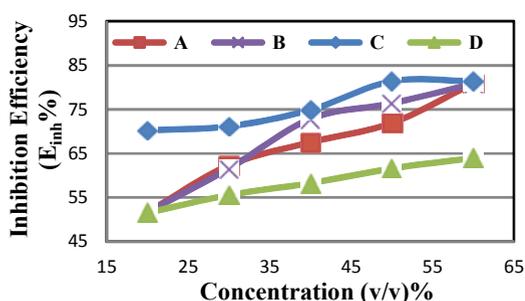


Fig. 2: Effect of extracts concentrations on inhibition efficiency (E_{inh} %)

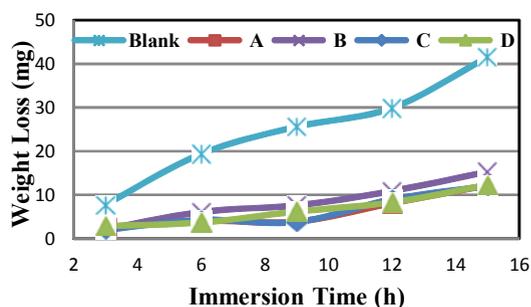


Fig. 3: Effect of immersion time on weight loss of carbon steel

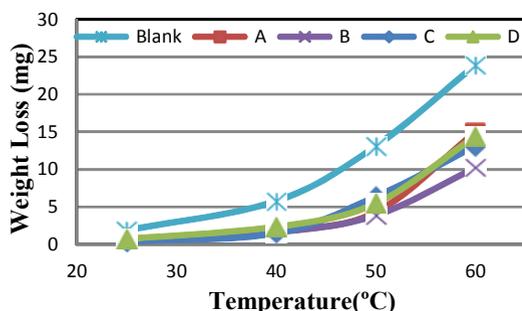


Fig. 4: Effect of temperature on weight loss of carbon steel

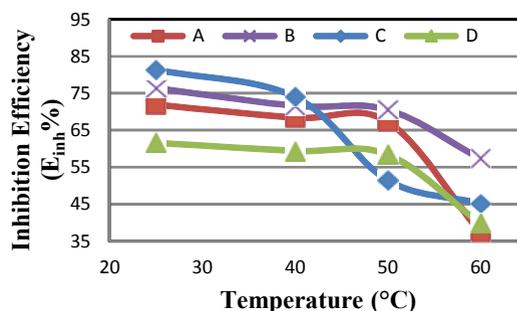


Fig. 5: Effect of temperature on inhibition efficiency of carbon steel

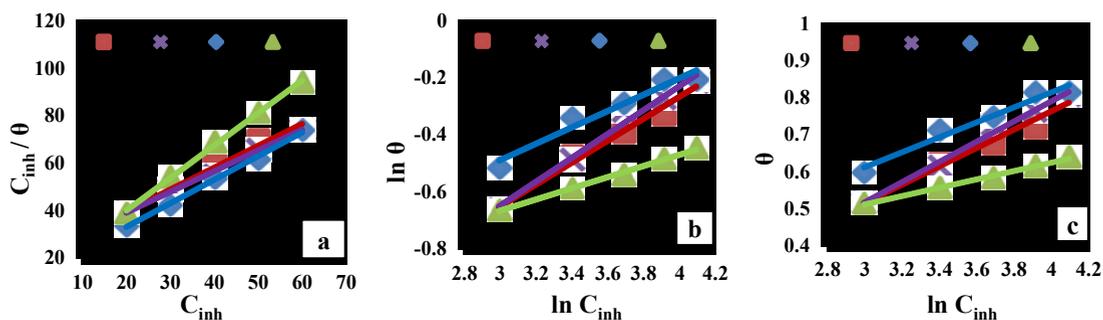


Fig.6: Langmuir (a), Freundlich (b), Temkin (c) isotherms for the adsorption of *GLV* extract on the surface of the carbon steel

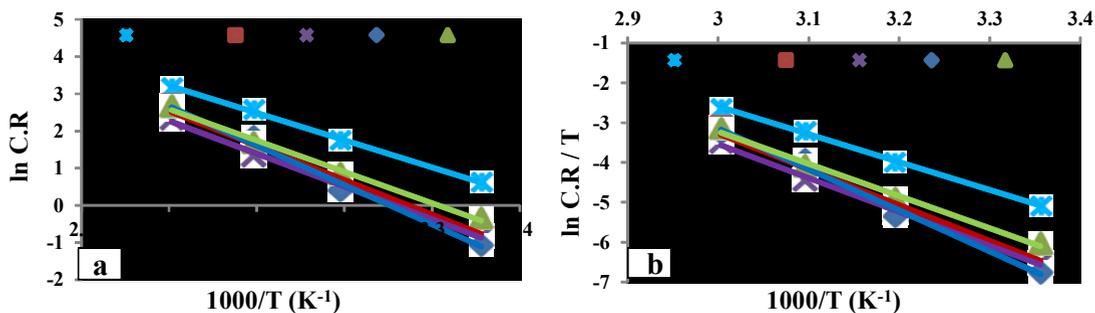


Fig. 7: Arrhenius (a), Transition state (b) plots for carbon steel in 1 M HCl at absence and presence of 50% GLV extract

showing that the reaction is spontaneous²⁷ and that the GLV extracts are strongly adsorbed on the carbon steel surface by physical adsorption.

Generally, the values of ΔG_{ads}° of up to -20 kJ/mol are consistent with electrostatic interaction between charged inhibitor molecules and the carbon steel surface (physical adsorption) and those more than -40 kJ/mol involves charge sharing or transfer from the inhibitor molecule to carbon steel surface to form a coordinate bond (chemisorption). In the present study, the values of the ΔG values which are less negative than -20 kJ/mol for various inhibitors concentrations (Table 3) revealed the adsorption of the inhibitor on the metal surface confirms a physical adsorption mechanism^{32, 36, 37}.

The Langmuir, Freundlich, and Temkin isotherms being followed confirms a mixed adsorption mechanism owing to the spontaneity of the process. Thus, the GLV extract can be used to inhibit the carbon steel corrosion in 1 M HCl.

The activation energy can be calculated from Eq. 10:

$$\ln C.R_{inh} = \ln A - \frac{E_a}{RT} \quad \dots(10)$$

From Fig. 7(a) the slope $-E_a/R$ was obtained by plotting the $\ln i_{cor}$ of 1 M HCl in the absence and presence of 50% GLV versus $1/T$. The calculated activation energies, E_a , are listed in Table 4. There are three groups of E_a value according to the temperature effects on the inhibition efficiency [28];

1. $E_{inh}\%$ decreases with increase in temperature, E_a (inhibited solution) $>$ E_a (uninhibited solution).
2. $E_{inh}\%$ increases with increase in temperature, E_a (inhibited solution) $<$ E_a (uninhibited solution).
3. $E_{inh}\%$ does not change with temperature, E_a (inhibited solution) = E_a (uninhibited solution).

It is clear from Table 4, The value of the apparent activation energy (E_a) in the presence of an inhibitor is larger than that in the blank solution, that indicate adsorption of the inhibitor was physically adsorbed on the metal surface, and that agrees case 2. Higher values of E_a in the presence of inhibitor signify increases thickness of the double layer which enhances the E_a of the corrosion process³⁸, and a strong inhibitory action of GLV extracts.

The enthalpy of activation (ΔH_{ads}°) and the entropy of activation (ΔS_{ads}°) for the corrosion of carbon steel in 1 M HCl solution in the absence and presence of GLV were calculated from the Arrhenius equation:

$$\ln \left[\frac{C.R_{inh}}{T} \right] = \ln \left[\frac{R}{Nh} \right] + \left[\frac{\Delta S_{ads}^{\circ}}{R} \right] - \left[\frac{\Delta H_{ads}^{\circ}}{RT} \right] \dots(11)$$

where h is the Plank's constant (6.626176×10^{-34} Js) and N the Avogadro's number ($6.02252 \times 10^{23} \text{ mol}^{-1}$). A plot of $\ln C.R_{inh}/T$ versus $1/T$ gave a straight line (Fig. 7 (b)) with a slope of $\Delta H_{ads}^{\circ}/R$ and an intercept of $\ln(R/Nh) + \Delta S_{ads}^{\circ}/R$, from which the values of ΔS_{ads}° and ΔH_{ads}° were calculated and listed in Table 4. In both the systems, the positive

signs of enthalpies ΔH_{ads}° reflect the endothermic nature of the dissolution process.

The ΔS_{ads}° is negative in all cases except inhibitor *D* with ΔS_{ads}° value for the system without inhibitor being more negative. A negative ΔS_{ads}° is an indication that the corrosion process is controlled by activation complex³⁹⁻⁴¹. A closer look at the ΔS_{ads}° values shows that the values shift towards a positive direction in the presence of the extracts. A positive shift is due to the formation of the adsorbed layer on the metal surface, which is believed to increase disorder of the system. The inhibitor layer impede the liberation of hydrogen ions at the metal surface, causing increased disorderliness resulting in increased entropy of the system^{40, 42}. Also, the positive values of ΔS_{ads}° reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the leading force for the adsorption of the inhibitor onto the carbon steel surface.

CONCLUSION

The following conclusions may be drawn from this study:

- The results obtained from the gravimetric (weight loss) method demonstrated that the

GLV extracts acts as an effective inhibitor of Carbon steel corrosion in 1 M HCl, and the *Petroselinum crispum* (Parsley) represents the best inhibitors.

- Inhibition efficiency increases with the increase in the concentration of *GLV*, but decreases with immersion time, and rise in temperature.
- The adsorption of *GLV* on the carbon steel surface from 1 M HCl follows the Langmuir, Freundlich, and Temkin adsorption isotherms.
- The calculated values of ΔG_{ads}° , E_a , ΔH_{ads}° , and ΔS_{ads}° revealed that the adsorption process are spontaneous and endothermic, and the inhibitor molecules were adsorbed on the metal surface through physical adsorption mechanism .
- Consequently, all the results show that the *GLV* extracts can act as an inhibitor against the corrosion of carbon steel in the HCl medium.

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