The Inhibitive Effect Of Eucalyptus Camaldulenis Leaves Extract On The Corrosion Of Low Carbon Steel In Hydrochloric Acid

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Abstract:

The inhibition behavior of eucalyptus camaldulenis leaves extract on the corrosion of low carbon steel in 3M HCl solution have been investigated using the gravimetric technique, Five different concentrations (2, 4, 6, 8and 10) g/l of eucalyptus camaldulenis leaves extract were studded .It was shown that the presence of eucalyptus camaldulenis leaves extract inhibited the corrosion of low carbon steel in the test solutions and that the inhibition efficiency depended on the concentration of the plant extract and on the time of exposure of the low carbon steel samples in 3M HCl solutions containing the extract. The experimental data complied form of the Langmuir adsorption isotherm and the value and sign of the Gibb's free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the low carbon steel surface through a physical adsorption mechanism.

Keywords: *Corrosion rate, corrosion inhibition, low carbon steel, eucalyptus camaldulenis, adsorption mechanism, free energy of adsorption.*

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الخلاصة:

يهدف البحث الى دراسة تثبيط تاكل فولاذ الكاربون المنخفض في وسط حامضي من حامض الهيدروكلوريك بتركيز 3 مولاري باضافة مادة مستخلص اوراق كاليبتوس بتراكيز مختلفة (10,8,6,4,2) غرام لكل لتر الى المحلول وذلك باستخدام تقنية gravimetric. وقد اظهرت النتائج بأنّ وجود مستخلص اوراق كالبتوس camaldulenis نَعَ تآكلَ فولاذ الكاربون المنخفض في محلول الإختبارَ وحيث إعتمدتْ كفاءةَ المنعَ على تركيز مستخلص النباتَ وقتِ تعرّض عينات فولاذ الكاربون المنخفض في 3 مولاري من محلول حامض الهيدروكلوريك الذي يَحتوي على المستخلصَ .اثبتت الدراسة ان الية عمل هذا النوع من المثبط عبارة عن امتزاز تبعا لعلاقة (لانكمور للامتزاز) وان قيمة طاقة الامتزاز الحرة لكبس بينت ان جزيئات المثبط امتزت تلقائيا على سطح فولاذ الكاربون المنخفض من خلال ميكانيكية الامتزاز الفيزياوي.

الكلمات المفتاحية : نسبة تآكل ، مانع تآكل ، فولاذ الكاربون المنخفض ، كالبتوس ، ميكانيكية الامتزاز، طاقة الحرة للامتزاز.

Introduction:

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth. Most of the effective inhibitors are used to contain heteroatom such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface [1]

Mineral acids are extensively used for cleaning; pickling and de-scaling of metallic materials especially iron [2]. Hydrochloric acid attacks aggressively towards low carbon steel leading to material deterioration which cause decreased service life of the metal. Organic inhibitors are the best choice to meet out such problem and to reduce the corrosion attack [3]. Natural products such as extracts of easily available plants and trees have been used as eco friendly corrosion inhibitors. Plant extract contains several organic compounds which have corrosion inhibition abilities. The extracts from different parts of many plants have been reported as corrosion inhibitors in acidic media [4-9]. An umpteen numbers of natural products, Sida rhombifolia. L, Citrus aurantiifolia, Henna, Ginger, Piper Nigrum, Azadirachta Indica (Neem) and Thyme have been isolated from different parts of plants and trees and its applicability as corrosion inhibitors has been reported [10-16].

Steel and its alloys are widely used in industry and because of this their corrosion behavior study in different aggressive media is necessary. Acid solutions are used in the most important industrial applications in etching and acid cleaning [17]. Hydrochloric acid is widely used for the removal of rust and industrial acid cleaning, acid descaling and oil well acidising, because of the general aggressiveness of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials. Inhibitors are generally used for this purpose to control the metal dissolution. A number of studies have recently appeared in the literature on the topic of the corrosion of C- steel in acidic solutions [18]. The present study aimed to investigate the efficiency of the eucalyptus camaldulenis leaves extract as corrosion inhibitors for C- steel in acidic solutions (hydrochloric acid solution) by weight loss method, by geometric experiment, the effect of addition of different concentration inhibition of the eucalyptus camaldulenis leaves extract and the effect of temperature on the rate of corrosion in order to calculate some thermodynamic parameters related to the corrosion process.

Material And Method:

Low carbon steel specimens of following compositions were used for the experiment (wt %). The composition of the sample was analyzed using ARL 3460 Metal Analyzer, Optical Emission Spectrometer.The chemical composition of the specimen is given in **Table 1:**

Table 1: Chemical Composition of Low Carbon Steel

Elements	Element concentration (Wt.%)	Elements	Element concentration (Wt.%)
C	0.0716	W	0.0141
Si	0.0023	Le	0.003
Ma	0.276	Sn	0.0044
P	0.0166	As	0.0102
S	0.0179	Zr	0.0015
Ch	0.0188	Bi	0.004
Mo	0.002	Ca	0.00047
Ni	0.0124	Ce	0.003
Al	0.0131	Bo	0.0002
Co	0.0015	Zn	0.002
Cu	0.0126	La	0.001
No	0.0019	Fe	99.5
Ti	0.001	Va	0.00079

Rectangular samples of area 2x4 cm^2 and thickness of 0.7 cm have been cut from a large sheet of low carbon steel. The samples were polished; the coupons were degreased by washing them in absolute ethanol, rinsed in acetone and allowed to dry. The dried coupons were stored in moisture free desiccators until required for use.

The chemicals and reagents used in this study were of analytical grade and distilled water was used to prepare them.

Preparation of Plant Extract:

Use of inhibitors is an important task in the protection of metals from corrosion. Till now the majority of metal corrosion inhibitors used is toxic for human being and environment. The choice of the present inhibitors is based on the following considerations:

- Less-expensive
- Non toxic
- Possess no threat to the environment
- Easy availability

For the present study, extract of eucalyptus camaldulenis are used as corrosion inhibitor for low carbon steel in hydraulic acid. The leaves were collected from a farm in AL-Adhamyia garden. The tested extracts were prepared by boiling weighed amounts of the dried and ground leaves of eucalyptus camaldulenis for one hour in one liter bidstilled water and left overnight. Then, the solution was filtered and stored. The concentrations of the extracts are expressed as (g/l).

Gravimetric Experiment

The sample coupons of low carbon steel were first weighed using a digital weighing balance OHAUS model AR.2140 with a least count of 0.0001 g, labeled and suspended in the test solutions (3 M HCl) with and without inhibitor. In the case where the variation of corrosion rate of metal with inhibitor concentration was desired, each coupon was allowed to stay in the test solution for 3 hours at different temperature (25-55) °C. After immersion, the sample coupon was cleaned, washed in distilled water several time, degreased in ethanol and dried in acetone. Further drying of the coupon was done by means of a hand dryer and then reweighed on cooling in order to determine the weight loss of the coupon. The corrosion rate was calculated by using the expression [19].

$$\text{Corrosion Rate} = \frac{KW}{DAT} \qquad (1)$$

Where
K = Rate constant equal to 534 mpy; mpy means mils per year; 1 mil = 10^{-3} in.
W = Weight loss in mg.
D = Density of material in gcm^{-3}.
T = Exposure time in hours.
A = Exposed area of coupon in in^2, noting that $1in^2 = 6.5416\ cm^2$.
The inhibition efficiency of the eucalyptus camaldulenis leaves extract on the corrosion of the low carbon steel in 3 M HCL containing different Concentrations of the eucalyptus camaldulenis leaves extract was computed by using the relation [20-21].

$$I\% = \left(1 - \frac{CR_{inh.}}{CR_{Blank}}\right) \times 100 \qquad (2)$$

Where $CR_{inh.}$ is the corrosion rate in the presence of the inhibitor while CR_{blank} is the corrosion rate in the absence of inhibitor.

RESULTS AND DISCUSSION

Corrosion Rate And Corrosion Inhibition

The corrosion rate of the low carbon steel in 3 M HCl in the absence and presence of eucalyptus camaldulenis leaves extract were determined at different temperature (25-55) °C. **Figure (1)** shows the time variation of corrosion rates of the low carbon steel in 3 M HCl without and with eucalyptus camaldulenis leaves extract at different concentration in (g/l), while **Figure (2)** shows the variation of the corrosion rates of the low carbon steel in 3 M HCL

with inhibitor concentration for an exposure time from (3) hours at different temperature (25-55) °C. The two Figures show clearly that the eucalyptus camaldulenis leaves extract retards the corrosion rate of the low carbon steel in the test solutions. Moreover, it can be seen from **Figure (2)** that the corrosion rate decreases with increase in the concentration of the inhibitor and increase with increase temperature at constant concentration.

Table (2) displays the corrosion rates of low carbon steel in 3 M HCL with and without eucalyptus camaldulenis leaves extract for different exposure times. It also shows the inhibition efficiency of eucalyptus camaldulenis leaves extract at different concentration in (g/l) of the corrosion of low carbon steel in 3 M HCL at different exposure times. Clearly, the inhibition efficiency of eucalyptus camaldulenis leaves extract decreases with exposure times for the inhibitor concentration considered. This result as shown in **Figure (3)** the inhibition efficiency increases with increase of the inhibitor concentration, tending to saturate at (6 g/l) value of inhibitor concentration at each temperature. This indicates that the effectiveness of the eucalyptus camaldulenis leaves extract in retarding the corrosion rate of low carbon steel in the test solutions does not improve indefinitely with increase in inhibitor concentration. A point is reached at which an increase in the inhibitor concentration produces only a very small increase in inhibition efficiency. A similar conclusion has been reached by [23] who studied the inhibitive effect of thiosemicarbozides on the corrosion of steel in phosphoric acid.

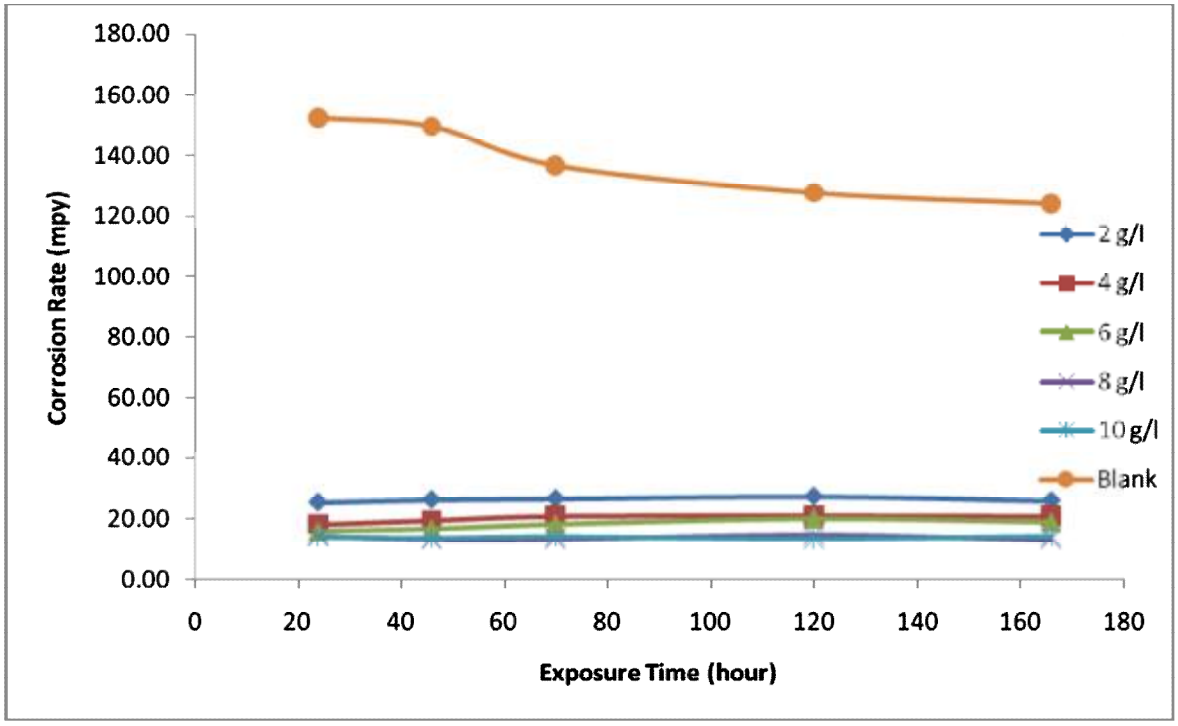

Fig. (1): Time variation of the corrosion rates of low carbon steel in 3M HCl.

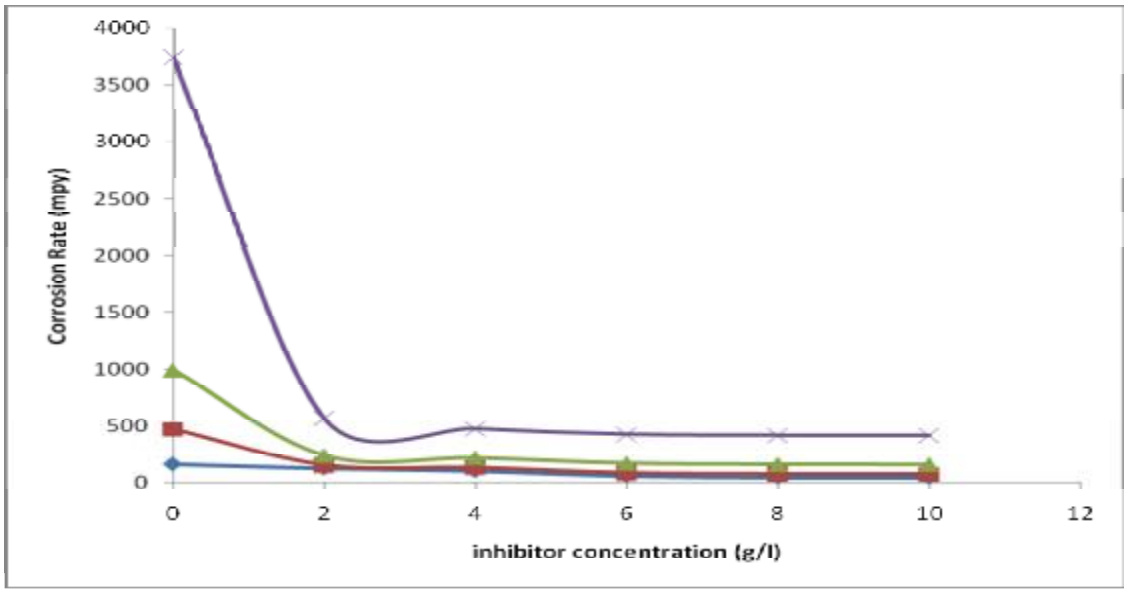

Fig. (2): Variation of corrosion rate of low carbon steel in 3 M HCl with different concentrations of eucalyptus camaldulenis leaves extract for exposure time 3 hours.

Table 2: Time variation of corrosion rate and inhibition efficiency for low carbon steel in 3 M HCl with inhibitor concentration in (g/l) of eucalyptus camaldulenis leaves extract and without the leaves extract.

Time (hour)	Corrosion rate (mpy)						Inhibition efficiency (I%)				
	Blank	2 (g/l)	4 (g/l)	6 (g/l)	8 (g/l)	10 (g/l)	2 (g/l)	4 (g/l)	6 (g/l)	8 (g/l)	10 (g/l)
24	152.7	25.5	18.3	16.0	14.4	14.1	83.3	88.0	89.5	90.5	90.7
46	149.9	26.4	19.6	16.9	13.4	13.7	82.4	86.9	88.8	91.0	90.9
70	137.0	26.7	20.9	18.4	13.5	14.2	80.5	84.7	86.6	90.1	89.6
120	127.7	27.5	21.1	20.3	14.7	13.4	78.5	83.5	84.1	88.4	89.5
166	124.1	26.0	21.0	19.1	13.3	14.4	79.1	83.2	84.6	89.2	88.4

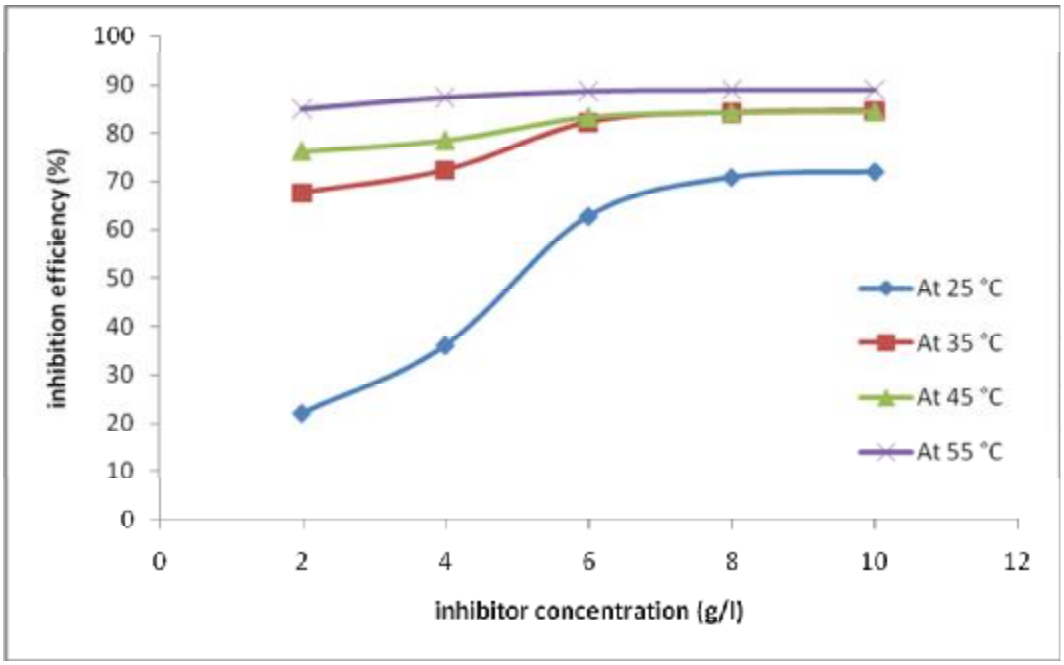

Fig. (3) . Variation of inhibition efficiency with concentration of eucalyptus camaldulenis leaves extract for low carbon steel in 3 M HCl for 3 hours at different temperature.

Table 3: Variation of the inhibition efficiency of eucalyptus camaldulenis leaves extract with concentration of inhibitor for low carbon steel in 3M HCL for 3 h.

inhibitor Concentration (g/l)	Corrosion rate (mpy)				Inhibition efficiency (I%)			
	25°C	35 °C	45 °C	55 °C	25 °C	35 °C	45 °C	55 °C
Blank	159.46	469.1	993.8	3739.8	-	-	-	-
2	124.23	152.1	235.5	567.4	22.1	67.6	76.3	84.8
4	101.98	129.8	213.2	474.7	36.1	72.3	78.5	87.3
6	59.33	83.44	166.9	424.6	62.8	82.2	83.2	88.7
8	46.35	74.17	157.6	415.3	70.9	84.2	84.1	88.9
10	44.50	72.31	155.8	413.5	72.1	84.6	84.3	88.9

Inhibitory Behavior of Eucalyptus Camaldulenis Leaves Extract:

The result that the inhibition efficiency of eucalyptus camaldulenis leaves extract increases with increase in inhibitor concentration suggests that some of the molecules of the inhibitor are adsorbed on the metal surface thereby protecting the "covered" surface from further corrode attack. Increasing the inhibitor concentration increases the degree of surface coverage, θ, of the metal surface defined as:

$$\theta = 1 - \frac{CR_{inh.}}{CR_{blank}} \qquad (3)$$

Eucalyptus is a natural organic compound which is a cyclic ether and a monoterpenoid. Eucalyptol is also known by a variety of synonyms: 1,8-cineol, 1,8-cineole, limonene oxide, cajeputol, 1,8-epoxy-p-menthane, 1,8-oxido-p-menthane, eucalyptol, eucalyptol, 1,3,3-trimethyl-2-oxabicyclo[2,2,2]octane, cineol, cineole.

Eucalyptus forms crystalline adducts with halogen acids, o-cresol, resorcinol, and phosphoric acid it is not possible at this point to identify

In any case, the adsorbate molecules on the metal surface constitute a barrier to charge and mass transfer between the metal and the corrodent, thereby protecting the metal surface from corrodent attack. The larger the degree of surface coverage resulting from enhanced adsorption of molecules of the plant extract, the greater the protection to corrosion offered by the inhibitor [21].

Adsorption Isotherms

In the situation where it is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of molecules of plant extracts onto the metal surface, it is instructive to investigate the possible adsorption mode by testing the experimental data obtained with several adsorption isotherms. Such an exercise will greatly elucidate one's understanding of the corrosion inhibition mechanism. This was been done in this study. The generalized expression for several adsorption isotherms usually tested is of the form [23-25].

$$f(\theta, x)\exp(-\alpha\theta) = KC \qquad (4)$$

Where f (θ, x) is the configuration factor whose functional form depends on the physical model adopted and assumptions made in deriving the isotherm,θ is the degree of surface coverage, x is known as the size ratio which gives the number of water molecule replaced by the inhibitor molecule, α is a molecular interaction parameter whose value depends on the type

of molecular interactions in the adsorption layer and the degree of homogeneity of the surface, C is the inhibitor concentration while K is the adsorption equilibrium constant which is temperature dependent according to the relation [23,24,26,27].

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G^{\circ}_{ads}}{RT}\right) \quad (5)$$

Where ΔG°_{ads} is the standard free energy of adsorption, R, is the molar gas constant and T is absolute temperature & the value 55.5 is the concentration of water in mol/l.

Several adsorption isotherms were tested for fit with the experimental data. These include the Langmuir, Frumkin, Temkin, Freundlich and the Flory-Huggins isotherms. Incidentally, the Langmuir isotherm gave the best fit with the experimental data. The Langmuir isotherm equation is of the form [21, 24, 25, 33].

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (6)$$

Figure (4) shows the Langmuir isotherm plot for the inhibition of the corrosion of low carbon steel in 3 M HCL by eucalyptus camaldulenis leaves extract. Using the value of intercept obtained from the graph and equations 3 and 4 a value are given in **Table (4).** The very good fit of the experimental data with the Langmuir adsorption isotherm suggests that the Langmuir adsorption model is applicable in the corrosion inhibition mechanism. In the derivation of the Langmuir isotherm, it was assumed that the adsorption sites on the metal surface are uniformly distributed and energetically identical and that the maximum number of adsorbed molecules per site is one, implying a case of monolayer adsorption. Additionally, it was assumed that adsorbate molecules do not interact with one another. The negative value of ΔG^{o}_{ads}, the Gibb's free energy of adsorption, obtained means that the adsorption process was spontaneous. The value of ΔG^{o}_{ads} obtained in this study is low enough for one to attribute the adsorption process as due to an electrostatic interaction between the atoms/ions on the metal surface and the adsorbate molecules [28], a mechanism which is consistent with physical adsorption (physiosorption). Values of ΔG^{o}_{ads} up to -20 kJ/mol are consistent with physical adsorption. The interactions involved in this mechanism are more or less weak electrostatic interactions between metal atoms and adsorbate species. In fact, the adsorption energies involved have the same range of energy values as the van der Waals bond energies [28]. However, values of ΔG^{o}_{ads} which are more negative than - 40 $kJmol^{-1}$ are associated with chemical adsorption, also called chemisorption. The mechanism involves charge sharing or charge transfer between the atoms of the metal and the adsorbate molecules. The associated bonds are strong and the corresponding bond energies could be as large as those characteristics of primary bonds in solids [28].

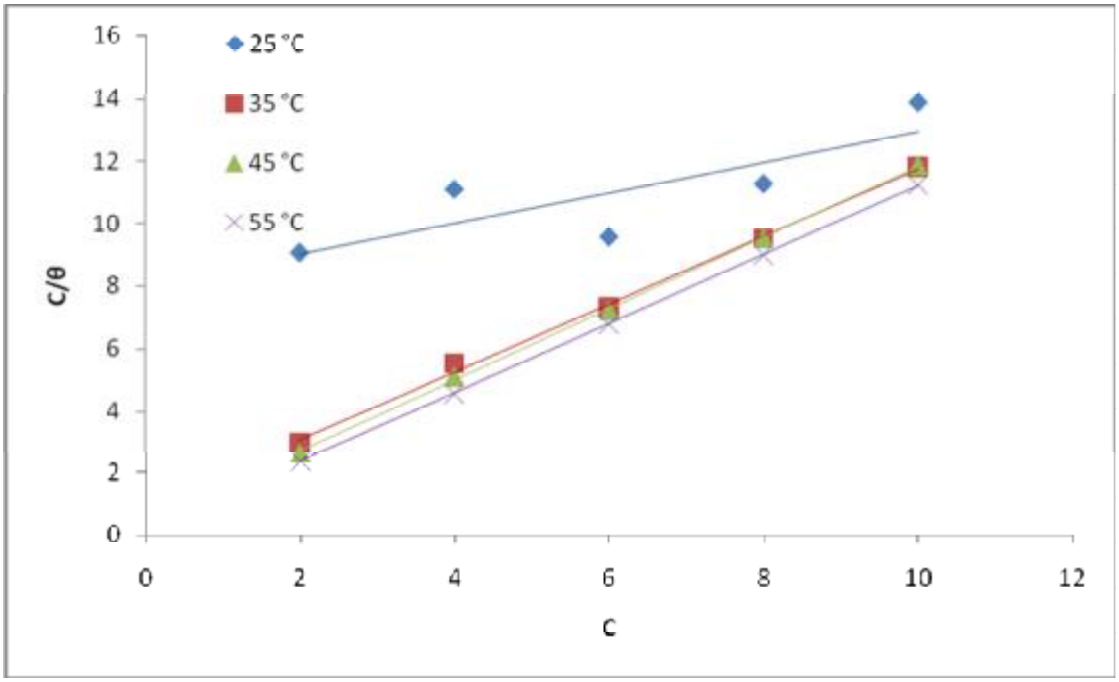

Fig. (4). Langmuir adsorption isotherm for inhibition of corrosion of low carbon steel in 3 M HCl by eucalyptus camaldulenis leaves extract.

The negative sign implies that the adsorption of the inhibitor onto the mild steel surface is a spontaneous process. The value indicates that the adsorption is physical. If the values of is in the order of -20 kJ/mole or less this would indicate a physical adsorption, while those values of -40kJ/mole or higher imply chemical adsorption which involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a physical bond [29].

Table 4: Equilibrium constant and adsorption free energy of the eucalyptus camaldulenis leaves extract adsorbed on C- steel surface corrosion in 3 M HCl.

Temperature (°C)	Kads	ΔG°ads ($kJ.mol^{-1}$)
25	0.1246	-4.791
35	1.096	-10.519
45	2.5575	-13.101
55	7.518	-16.453

Thermodynamic parameters obtained from Gibbs-Helmholtz equation according to this equation [22]:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (7)$$

Plots of ΔG°_{ads} vs. T for adsorption of the used compounds on the surface of C- steel in 3 M hydrochloric acid over the temperature range from 25 °C to 55 °C are shown in (Fig. 5). The data gave straight lines of intercept ΔH°_{ads} and slope ΔS°_{ads}. The value of ΔH°_{ads}=106.3 kJ/mol & ΔS°_{ads} =375 J/mol.K from **Figure (5).**

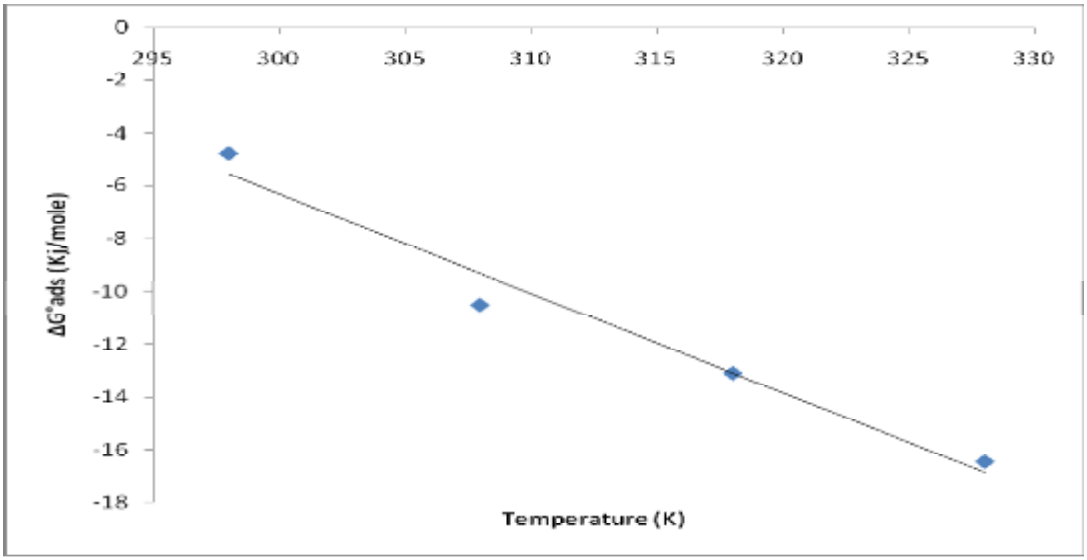

Fig. (5): The free energy of adsorption ΔG_{ads} for corrosion of C – steel in 3 M HCl in presence of the inhibitors investigated at different temperatures.

Effect of temperature

The effect of temperature on the corrosion rate of low carbon steel in free acid and in the presence of different concentrations of eucalyptus camaldulenis leaves extract was studied in the temperature range of 25–55 °C using weight loss measurements. In examining the effect of temperature on the corrosion process in the presence of the exudates, the Arrhenius equation below was used [30]:

$$\text{Log CR} = \text{Log A} + \frac{-E_a}{2.303\ RT} \qquad (8)$$

Where 'CR' is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. **Figure (6**) represents Arrhenius plot (as log CR versus 1/T) for low carbon steel corrosion in 3 M HCl in the absence and presence of various concentrations of eucalyptus camaldulenis leaves extract. Straight lines were obtained with slope equals to ($-E_a/2.303R$). The values of E_a for the corrosion reaction in the absence and presence of eucalyptus camaldulenis leaves extract were

calculated and are presented in **Table (6).** Inspection of the Table shows that the presence of the eucalyptus camaldulenis leaves extract decrease the value of Ea when compared to the blank (3 M HCl) indicating the adsorption of eucalyptus camaldulenis leaves extract on the surface of the metal. The higher value of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to its physisorption, while the opposite is the case with chemisorption [31, 32].

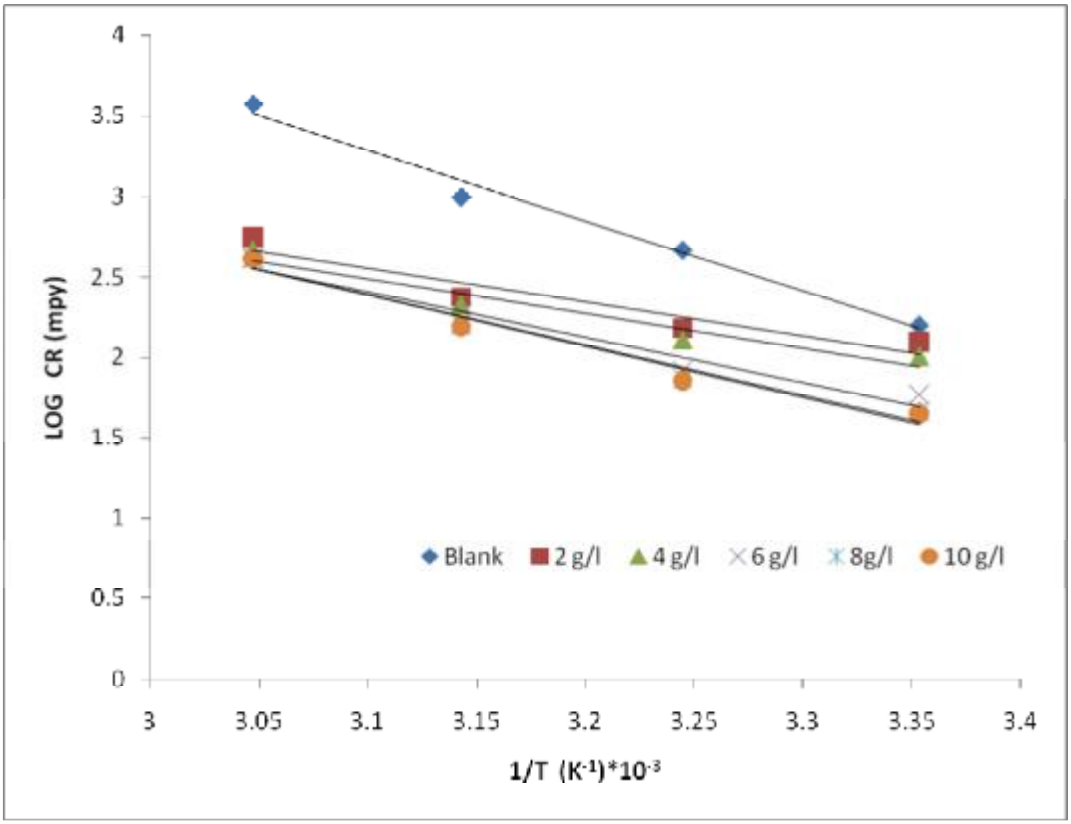

Fig. (6): Arrhenius plot (as log CR versus 1/T) for low carbon steel corrosion in 3 M HCl in the absence and presence of various concentrations of eucalyptus camaldulenis leaves extract.

Table (6): Activation Energy Ea (kJ/mol) for low carbon steel corrosion in the presence of eucalyptus camaldulenis leaves extract in 3 M HCl

Concentration (g/l)	Ea (kj/mol)
Blank	8.292
2	4.024
4	4.124
6	5.332
8	5.935
10	6.035

Conclusions

1. Eucalyptus camaldulenis leaves extract acts as an inhibitor for corrosion of low carbon steel in 3 M HCl solution.
2. The inhibition efficiency increases with increase in the concentration of eucalyptus camaldulenis leaves extract and increase with increase in temperature.
3. The inhibition is due to the presence of some phytochemical constituents in the Eucalyptus camaldulenis leaves extract which is adsorbed on the surface of the low carbon steel metal.
4. The Eucalyptus camaldulenis leaves extract was found to obey adsorption isotherm and kinetic–thermodynamic model from the fit of experimental data.
5. The values of ΔG^{o}_{ads} are negative which suggest that the inhibitors were strongly adsorbed on the low carbon steel metal surface. The values obtained support the physical adsorption mechanism.
6. Thermodynamic parameters revealed that adsorption process is spontaneous.

References

1. **Ambrish Singh, Eno E. Ebenso, and M. A. Quraishi" Corrosion Inhibition of Carbon Steel in HCl Solution by Some Plant Extracts" International Journal of Corrosion Volume 2012 (2012), Article ID 897430, 20 pages**
2. **Farina, C.A., Faita, G. & Olivani, F. (2004), Electrochemical Behaviour of Iron in Methanol and Dimethylformamide solution,Corrosion Science (18), 463-479.**
3. **Schmitt G, (1994), Inhibitors for chemical cleaning treatment in corrosion inhibitors, Working Party Report – II;" Inst. of Materials, London, 64-91.**
4. **Okafor, P.C., Ikpi, M.E., Uwah, I.E., Ebenso, E.E., Ekpe, U.J. & Umoren, S.A., (2008), Inhibitory action of phyllanthus amarus extract on the corrosion of mild steel in acid media,Corros. Sci. 50, 2310-2317.**
5. **Ebenso, E.E. & Ekpe, U. J., (1996), Kinetic study of corrosion and corrosion inhibition of mild steel in H2SO4 using Carica papaya leaves extract. W. Afr. J. Bio. Appl. Chem. 41, 21-27.**
6. **Kliskic, M., Radosevic, J., Gudic, S. & Katalinic, V., (2000). Acqueous extracts of Rosmarines officinalis L as corrosion inhibitor of Al-Mg alloys corrosion in chloride solution, J. Appl. Electrochem. 30, 823-823.**
7. **Ebenso, E.E., Ibok, U. J., Ekpe, U. J., Umoren, S., Jackson, E., Abiola, O. K., Oforka, N. C. & Martinez, S., (2004), Corrosion inhibition studies of some plant extracts on aluminium in acidic medium. Trans. of SAEST ,39, 117-123.**

8. **El-Etre A.Y., Abdallah M. & El-Tantawy Z.E., (2005), Corrosion inhibition of some metals using lawsonia extract. Corros. Sci., 47, 385-395.**
9. **Umoren S.A., Obot I. B., Ebenso E. E., Okafor P. C., Ogbobe O. & Oguzie E. E., (2006), Gum arabic as a potential corrosion inhibitor for aluminium in alkaline medium and its adsorption characteristics , Anti-Corros. Meth. Mater. 53, 277-282.**
10. **Saratha. R & Meenakshi. R, "Corrosion inhibitor-A plant extract" Der Pharma Chemica, 2(1): 287-294. (2010).**
11. **Saratha R., Priya S.V. & Thilagavathy P., "Investigation of Citrus aurantiifolia Leaves Extract as Corrosion Inhibitor for Mild Steel in 1M HCl" E-Journal of Chemistry, 6(3), 785-795. (2009).**
12. **Chetouani A. & Hammouti B., "Corrosion inhibition of iron in hydrochloric acid solutions by naturally henna" Bull Electrochem 19, 23-25. (2003).**
13. **Bouyanzer A. & Hammouti B., "Naturally occurring ginger as a corrosion inhibitor for steel in molar hydrochloric acid at 353 K "A. Bull. Electrochem., 20, 63-65. (2004).**
14. **Anand B. & Balasubramanian, V. "A comparative study on corrosion inhibition of mild steel using Piper Nigrum L. in different acid media", E-Journal of Chemistry, 7(3), 942-946. (2010).**
15. **Peter C. Okafor, Eno E. Ebenso & Udofot J. Ekpe," Azadirachta Indica Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium" , Int. J. Electrochem. Sci., 5, 978 – 993. (2010).**
16. **Bendahou, M., Benabdallah, M. & Hammouti, B., "A study of rosemary oil as a green corrosion inhibitor for steel in 2M H_3PO_4", Pigm Res Technol. 35 (2), 95-100. (2006).**
17. **A.Cojocaru, I.Maior, D.I.Vaireanu, C.Lingvay, I.Lingvay, S.Caprarescui, G.E.Badea "Ethanol Extract of Fagus Sylvatica leaves as an eco-friendly inhibitor for carbon steel corrosion in acidic solutions" Journal of sustaninable energy, Vol. 1, No. 3, Septemper, 2010**
18. **M.Abdallah1,3 , Basim H. Asghar1, I. Zaafarany1, and A.S.Fouda" The Inhibition of Carbon Steel Corrosion in Hydrochloric Acid Solution using Some Phenolic Compounds" International Journal of electrochemical science 7 (2012) 282 – 304**
19. **Callister WD Materials Science and Engineering: An Introduction, John Wiley and Sons Inc. New York, p. 579. (2003).**
20. **Oguzie EE, Onuoha GN, Ejike EN "Effect of Gongronema latifolium extract on aluminium corrosion in acidic and alkaline media" Pigment Resin Technol., 36(1): 44-49. (2007).**

21. **Oguzie EE "Corrosion inhibitive effect and adsorption behavior of Hibiscus sabdariffa on mild steel in acidic media" Portugaliae Electrochemica Acta., 26: 303-314. (2008a).**

22. **Oguzie EE "Evaluation of some inhibitive effect of some plant extracts on the acid corrosion of mild steel" Corros. Sci., 50: 2993- 2998. (2008b).**
23. **Ameer MA, Khamis E, Al-Sanani G "Adsorption studies of the effect of thiosemicarbazides on the corrosion of steel in phosphoric acid" Adsorpt. Sci. Tech., 18: 177-194(2000).**
24. **Iannuzzi M, Frankel GS "Mechanisms of corrosion inhibition of AA2024-T3 by vanadates" Corros. Sci., 49: 2371-2391. (2007).**
25. **Ebenso EE, Eddy NO, Odiongenyi AO "Corrosion inhibition and adsorption properties of methacarbanol on mild steel in acidic medium" Portugaliae Electrochemica Acta., 27(1): 13-22. (2009).**
26. **Martinez S "Inhibitory mechanism of mimosa tannin using molecular modelling and substitutional adsorption isotherms." Mater. Chem. Phys., 77: 97-102. (2002).**
27. **Emregul KC, Hayvali M "Studies on the effect of vanillin and protocatechualdehyde on the corrosion of steel in hydrochloric acid" Mater. Chem. Phys., 83: 209-216. (2004).**
28. **Raghavan V ,Materials Science and Engineering: A First Course. Third Edition. Prentice – Hall of India Private Limited, New Delhi. (1989).**
29. **M. Donahue and K. Nobe: *J. Electrochem. Soc*. 112 (1965) 886.**
30. **I. N. Putilova, S. A. Balezin and V. P. Barannik, Metallic Corrosion Inhibitors, Pergamon Press, New York (1960) 31.**
31. **M. Elayyachy, B. Hammouti and A. El Idrissi, New telechelic compounds as corrosion inhibitors for steel in 1M HCl, Appl. Surf. Sci. 249 (2005) 176–182.**
32. **M.S. Morad, A.M. Kamal, El - Dean, 2,2‘- Dithiobis (3-cyano-4,6-dimethylpyridine): A new class of acid corrosion inhibitors for mild steel, Corros. Sci. 48 (2006) 3398–3412.**
33. **Eddy NO, Ebenso EE "Adsorption and inhibitive properties of ethanol extract of Musa sapientum peels as a green corrosion inhibitor for mild steel in H_2SO_4"Afr. J. Pure Appl. Chem., 2(6): 46 - 54. (2008).**