*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

# Study Of Corrosion Inhibition Effect Of Punica – granatum Fruit – Shell Extract On Carbon Steel In 0.5M Hydrochloric Acid Solution

**Adnan S. Abdul Nabi and Luma Taher Tuma Albaaj**

**Chemistry Department, College Of Education, University Of Basrah**

https://doi.org/10.32792/utq/utj/vol19/2/2

## Abstract

Naturally occurring substances are increasingly being tried as corrosion inhibitors of metals in acid cleaning processes to replace some toxic and expensive chemicals currently in use. The inhibitive action of ***Punica – granatum*** fruit – shell extract was investigating in 0.5M Hydrochloric acid by weight loss measurements. The work showed that the additive retarded the dissolution of carbon steel to an extent depending on the concentration of the additive. The surface coverage (θ) data augment the above observation and the inhibition is attributed to the physical adsorption of the chemical components of the additive on the surface of the carbon steel. Inexpensive environmentally safe inhibitor formulations indicate have been obtained.

## Introduction:

Metals and its alloy are exposed to the action of acids in industry [(1)]. Processes in which acids play a very important part are acid pickling, industrial acid cleaning of oil refinery equipment, oil well acidizing and acid descaling [(1,2)]. The exposures can be most severe but in many cases, corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates of metallic materials

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

in these acid media [2,3]. Because of the toxic nature and high cost of some chemicals currently in use it is very important to choose cheap and safely handled compounds to be used as corrosion inhibitors. Natural products of plant origin contain various organic compounds, e.g. organic and amino acids, alkaloids, tannins, pigments and most of these constituents are known to have inhibitive action [4,5].

The present paper reports on the corrosion inhibition of carbon steel in HCI solution by the aqueous extract of ***Punica granatum*** fruit – shells. The ***Punica granatum*** contains different compounds like, Bioncyn, Granatunin, Grantin, resins, Citric acid, Tannic acid, Mallic acid, Ellagic acid and Gallic acid [6] .

Literature survey reveals that not much study( ) has been carried out on inhibitory action of our local plants extracts. In view of the expanding research into possible corrosion inhibitors the present investigation has been taken up with an idea of understanding the mechanism and other aspects of the inhibition of carbon steel in HCI by the aqueous extract of ***Punica granatum*** fruit – shells using weight loss technique. The effect of temperature on the inhibiting action is also reported.

## Experimental:

The tested material was carbon steel type N – 80. The following table shows the composition of the N – 80.

| Material type | Composition |
|---|---|
| Carbon Steel | 0.25%C, 0.73%Mn, 0.18% Si, 0.028% S, 0.01% P, and Fe for balance. |

Table (1-1): Chemical composition of the material tested.

The ***punica granatum*** fruit-shell was shed dried at $25^0$C and then grounded with a blender and kept in nylon bags till to the tome of use. 50g. of dry fruit shell powder were shacked separately wieh 200ml. of disttiled water using electrical mixer with stirring for 24hrs. at room temperature. The residue was removed by filtration, and the filtrate was concentrated under vacuum by freeze drier to afford 8.3g of

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

dried extract[7] . The dreied extract should be stored in a refrigerator and a trace of toluene added to prevent fungal growth until used as a starting material [8].

Weight loss measurements were carried out with a metal specimens of carbon steel have a dimensions (7.2 x 2.2 x 0.3 cm). All the specimens are vacuum annealed at 500 $^{o}$C for 5h. after which they are allowed to cool at room temperature. The specimens are abraded under running tap water using emery paper of a grade numbers of 120, 400 and 600, washed with tap water followed by distilled water and then are dried with a clean tissue. Then, they are kept in a desiccators over a silica gel[9]. Each coupons were suspended by a glass hook and immersed in 200ml. beakers containing 0.1N HCI solution (Blank) and with additive concentration of 0.5%, 1%, 2%, 2.5% and 3% in 0.1N HCI solution at 25, 35 and 45$^{o}$C. The specimens weight are measured by electronic balance ( sartoius BL 210S ) and then suspended inside the solution. After 1h. in the solution, the specimens were raised from the solution, washed in tap water in order to remove all the corrosion products from the metal surface, washed again with distilled water, dried by clean tissue and then the specimens were weighed again after they have been kept in a desiccators over silica gel for 3hrs. . The same procedure was repeated for each temperature.

The corrosion rates (CR) for carbon steel have been determined from weight loss using the formula [10]:

$$\text{Corrosion Rate (mpy)} = \frac{534\ W}{D\ A\ T} \quad \text{---------- (1)}$$

Where:

W: is weight loss (mg).

D: density (g/cm$^3$).

A: area of the carbon steel coupon (inch$^2$).

T: exposure time (hour).

The additive percentage inhibition efficiency (%E) was determined from[11]:

$$\%E = \frac{CRo - CRi}{} \times 100 \quad \text{----------(2)}$$

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

CRo

Where:

CRo and CRi are the corrosion rates in the absence and presence of various concentrations of additive respectively.

## Results and Discussion:

Visual observation made on carbon steel coupons after 1hour exposures in 0.5M HCl solutions containing various concentrations of additive showed that the surface of carbon steel from each of the HCl solutions containing various concentrations of the additive was less corroded; than the surface of carbon steel in the HCl solution without additive ranging from bright grey steel surface to dull grey surface. However the surface of carbon steel from HCl solution without additive severe corrosion with very dull black carbon steel surface. The observation showed that the additive inhibited carbon steel dissolution in 0.5M HCl solution.

The corrosion rate decrease with increasing concentration of ***punica granatum*** fruit – shell extract at each of the temperature as shown in (Table 2). This confirms that the presence of the additive in 0.5M HCl solution inhibits the corrosion of carbon steel and the degree of inhibition depends on the amounts of ***punica granatum*** . The corrorsion rate as a function of additive concentration at different temperatures (25, 35and 45 $^{o}$C) is shown in Fig.(1), which confirms that the additive is a corrosion inhibitor; since there was a general decrease in corrosion rate (mpy) at each temperature.

Fig.(2) illustrate the variation of inhibition efficiency (%E), versus the concentration of the additive at (25,35,45$^{o}$C). The inhibition efficiency increase with increasing the concentration of the inhibitor. As shown in fig.(2) the inhibition efficiency increase with increase in concentration of the inhibitor up to 3% w/v at a maximum efficiency of 82%, 78% and 73.24% at 25$^{o}$C, 35$^{o}$C and 45$^{o}$C respectively.

From the plots of the inhibition efficiency with concentration of the inhibitor and from the results given in (Table 2), it was observed that with increase in temperature there was a decrease in the inhibition efficiency of the inhibitor. This indicates that inhibition decreases as temperature of the system increases, and on this basis we suggest the mechanism of physisorption of the inhibitor on the metal surface. This is in agreement with the results of several investigators[12 - 14].

Previous studies [15,16] have agreed upon that the overall reaction of iron dissolution is:

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

$Fe \longrightarrow Fe^{2+} + 2e^{-}$ ----------(3)

Therefore, the corrosion rate in current density units[17] can be related with the weight loss by equation (4):

$$Icorr.\ (mA/Cm^2) = \frac{2 \times 1000 \times W \times F}{Aw. \times t \times A} \quad \text{---------- (4)}$$

Where:

Icorr. = corrosion current density, ($mA/Cm^2$).

F = Faraday constant, 96500 coulombs.

Aw. = Atomic weight of iron, 55.9 .

T = Exposure time, (second).

A = External surface area of the specimen ($Cm^2$).

W = Weight loss due to corrosion (mg.).

Table (3) shows the variation of the values of the corrosion current density for the carbon steel specimen in 0.5M HCl solution with the temperature and inhibitor concentration. Values of icorr. for the carbon steel in acid solution in the absence of inhibitor are increased with increasing temperature from 25°C. This is because of the simulating of the anodic reaction with increasing temperature [1,15,18], which leads to increase the diffusion Coefficient of oxygen, since the studied system under partial diffusion control. Values of icorr. in the presence of inhibitor are increased with increasing temperature because the increasing of the temperature leads to increase the solubility of adsorbed layer which prevents the penetration of $H^+$ and $O_2$ to iron substrate.

The activation energy, Ea, was calculated by making use of the integrated form of the Arrhenius equation[12]:

$$Log \frac{K_2}{K_1} = \frac{Ea}{2.303\ R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{----------(5)}$$

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

Where:

Ea: Activation energy.

$K_2$ , $K_1$ : Corrosion rate at 50 & 40 $^oC$ respectively.

R: Gas constant.

$T_2$ , $T_1$ : the absolute temperature.

Table (3) shows the estimated of activation energy in the absence of inhibitor (33.77 KJ/mol), while in the presence of inhibitor are (67.85, 73.74, 83.86, 92.66, 53.16 KJ/mol) for (0.5,1,2,2.5,3 W/V%) of inhibitor concentration respectively. The deviation is may be attributed to the neglecting of the effect of temperature on the solubility of the adsorbed layer. The average activation energy value of (74.25KJ/mol) obtained in this study for the inhibition reaction confirms the assertion that the inhibition of corrosion of carbon steel is by physical adsorption mechanism. This result is in good agreement with the results of several investigators [19]. These reports indicate that the heat of chemical adsorption should greater than 80 KJ/mol. and a value less than this signifiers a physical adsorption mechanism. Also, for a chemical adsorption mechanism, inhibition efficiency increases with increase in temperature[19],whereas decrease in inhibition efficiency with increase in temperature is suggestive of a physical adsorption mechanism.

The surface coverage (θ) at each concentration of inhibitor, according to Damaskin [20] was determined using the equation:

$$\Theta = 1 - \frac{CRi}{CRo} \quad \text{---------- (6)}$$

Where CRo & CRi are the corrosion rates in the absence and presence of the inhibitor at various concentration of the ibhibitor.

Table (4) gives the calculated values of (θ) at different temperatures and inhibitor concentration. At constant temperature, θ is increased with increasing inhibitor concentration. On the other hand, the values of θ at a given inhibitor concentration is decreased with increasing temperature from 25$^oC$ to 45$^oC$.

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

The manner in which the values of θ for the inhibitor varied at a constant temperature with the concentration ( C ) of the inhibitor confirmed to Langmuir adsorption isotherm which may be expressed as[3]:

$$\frac{C}{\theta} = \frac{1}{b} + C \qquad \text{---------- (7)}$$

Where b is constant. A plot of C/θ values against the corresponding values of C is found to be linear as indicated in figure (3).

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

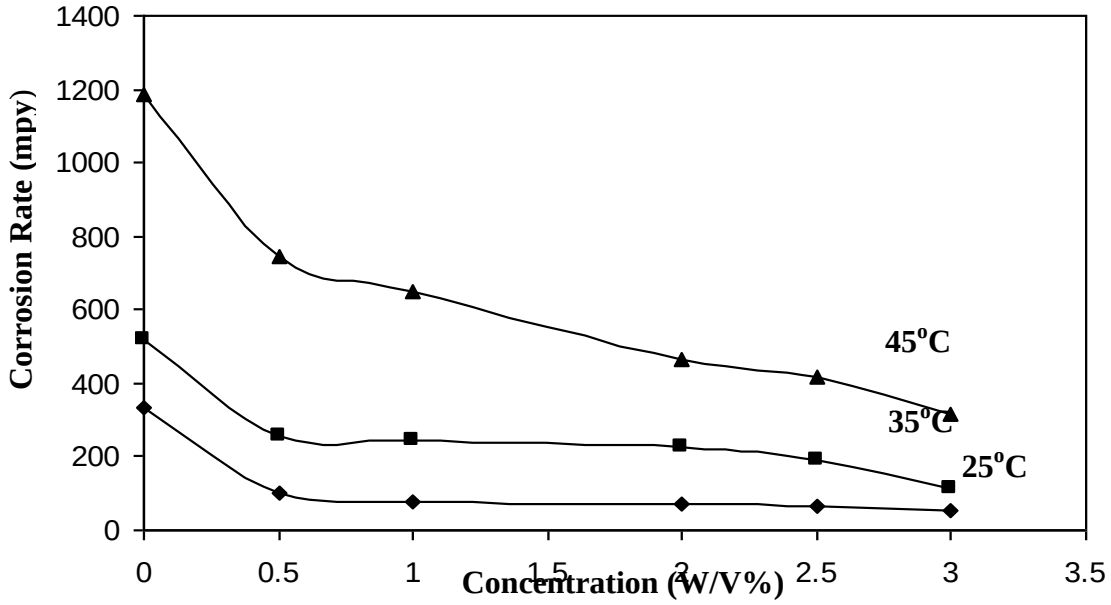


Figure (1): Variation of corrosion rate with various concentration of ***Punica granatum*** extracts for carbon steel coupons in 0.5M HCl solutions at 25°C, 35°C and 45°C.

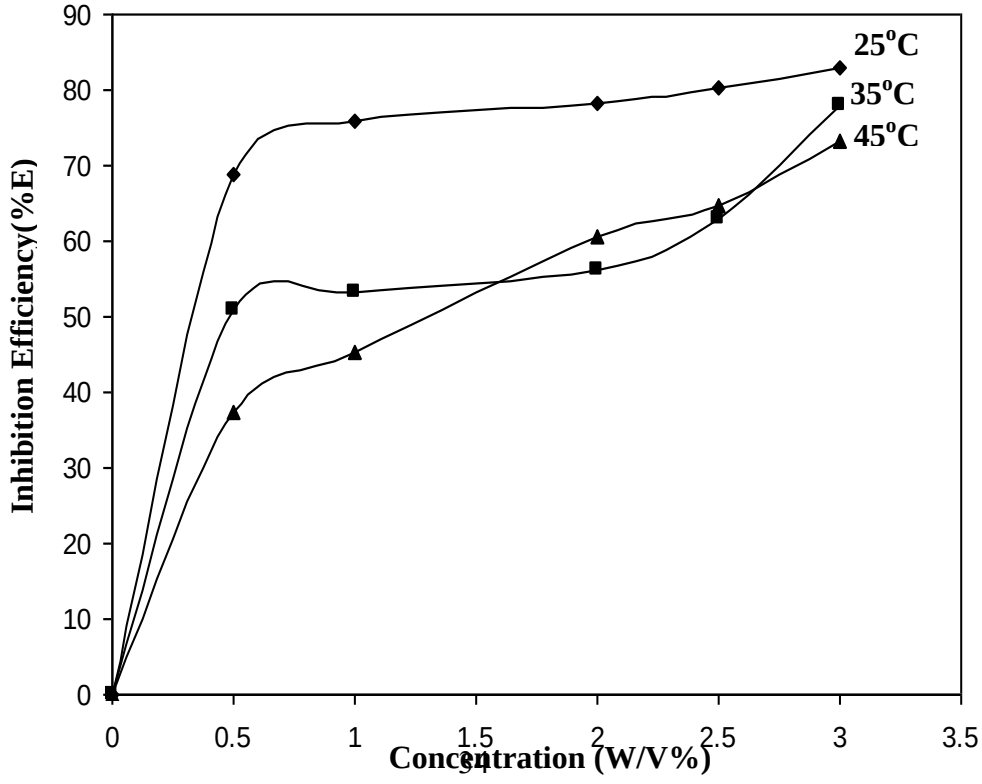


Figure (2): Variation of percentage Inhibition efficiency with various concentration of ***Punica granatum*** extracts for carbon steel coupons in 0.5M HCl solutions at 25°C, 35°C and 45°C.

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

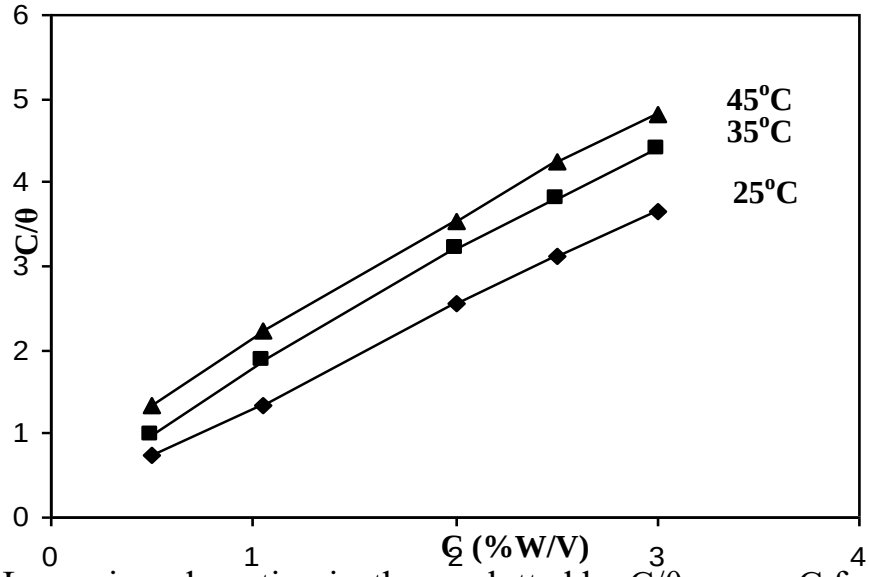


Figure (3): Langmiur adsorption isotherm plotted by C/θ versus C for ***Punica granatum*** extract in the carbon steel / 0.5M HCl system at 25°C, 35°C and 45°C.

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

Table(2): Percent inhibitor efficiency (%E) and corrosion rate (mpy) of carbon steel in 0.5M HCl solution containing various concentration of ***Punica granatum*** extract at different temperature.

| Conc. (w/v%) | Temperature (C) | | | | | |
|---|---|---|---|---|---|---|
| | 25 | | 35 | | 45 | |
| | mpy | %E | mpy | %E | mpy | %E |
| 0 | 331.20 | ---------- | 517.94 | ---------- | 1185.05 | ---------- |
| 0.5 | 103.35 | 68.79 | 253.68 | 51.02 | 742.27 | 37.36 |
| 1 | 79.86 | 75.86 | 241.94 | 53.28 | 647.13 | 45.93 |
| 2 | 72.03 | 78.25 | 226.67 | 56.23 | 466.26 | 60.65 |
| 2.5 | 65.47 | 80.23 | 191.44 | 63.03 | 416.94 | 64.81 |
| 3 | 56.37 | 82.98 | 113.92 | 78.00 | 317.10 | 73.24 |

Table( 3 ): Corrosion current densities (mA/cm$^2$) at different temperature and Activation Energy (KJ/mol.) of Carbon steel in 0.5M HCl at different inhibitor concentration of ***Punica granatum*** extract.

| Conc.(w/v%) | Icorr. (mA/Cm2) | | | Ea (KJ/mol.) |
|---|---|---|---|---|
| | 25C | 35C | 45C | |
| 0 | 724.68 | 1133.28 | 2592.94 | 33.77 |
| 0.5 | 537.06 | 555.07 | 1624.12 | 67.85 |
| 1 | 472.82 | 529.38 | 1415.96 | 73.74 |

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

*Vol.19 No.2 Dec 2024*

| | | | | |
|---|---|---|---|---|
| **2** | **310.94** | **495.97** | **1020.21** | **83.86** |
| **2.5** | **226.14** | **418.87** | **912.28** | **92.66** |
| **3** | **123.35** | **249.27** | **693.84** | **53.16** |

Table(4): Effect of Inhibitor concentration and Temperature on the surface coverage (θ) for the carbon steel specimen in 0.5M HCl

| **Conc. (w/v%)** | **Temperature (C)** | | |
|---|---|---|---|
| | **25** | **35** | **45** |
| **0.5** | **0.68** | **0.51** | **0.37** |
| **1** | **0.75** | **0.53** | **0.45** |
| **2** | **0.78** | **0.56** | **0.60** |
| **2.5** | **0.80** | **0.63** | **0.64** |
| **3** | **0.82** | **0.78** | **0.73** |

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

## Reference

1- C.C. Nathan, "Corrosion Inhibitors", ,Ed.,NACE,Houston, Texas,(1973).
2- S.S. Abd El-Rehim,M.A.M. Ibrahim and K.F. Khalid, Mater.Chem.& Physics, 70 (2001).
3- W.J.Moor,"Physical Chemistry", 5th Ed., (1972).
4- U.J.Ekpe, E.E.Ebenso and U.J.Ibok, K.W.Afri.Sci.Assoc.,37, (1994).
5- R.M.Saleh and A.M.Shams El-Din,Corro.Sci., 12, (1972).
6- النباتات الطبية والتداوي بلأعشاب، د. عبد الرضا علوان المياح, جامعة تعز، الجمهورية اليمنية، (2001) .
7- J.B.Iqbal, Ph.D.Thesis, College of Science, Basrah University, Iraq, (2001).
8- J.B.Harborne,"Phytochemical Methods", 2nd Ed., Chapman and Hall, London, UK,(1984).
9- O.K.Abiola and N.C. Oforka, J.of Corro.Sci. & Eng., 3, (2002).
10- R.S. Tredder, NACE, Houston, Texas, 7,(1984).
11- M.J.Danielson, J.Corro., (NACE), 11, (1982).
12- O.K.Abiola and N.C. Oforka, J. of Sci. Africana, 2, (2003).
13- A.Y. El-Etre, Corro. Sci., 40, (1998).
14- R.M. Saleh. A.A. Ismail and A.A. El-Hosary, Br. Corro. J., 17, (1982).
15- N. Shaker, M.Sc. Thesis, Univer. Of Technology, Baghdad, Iraq, (1986).
16- H.H. Uhlig and R.W. Revie, "Corrosion and Corrosion Control", 3rd Ed., John Wiliey, (1985).
17- S. Glasstone and D.Lewis, "Elements of Physical Chemistry", 2nd Ed.,Mac Millan Co.Ltd., (1960).
18- G. Adam, "Industrial Chemistry", Mosil University Press, Iraq, (1986).
19- U.J.Ekpe, U.J. Ibok, B.I. Ita, O.E. Offiong and E.E. Ebenso, Mter.Chem.Phys., 40, (1995).
20- B.B. Damaskin, "Adsorption of Organic Compounds on Electrodes", Plenum Press, New York, (1971).

*University of Thi-Qar Journal*

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

***Vol.19 No.2 Dec 2024***

# دراسة الفعل التثبيطي لمستخلص قشور الرمان على الفولاذ الكاربوني في محلول 0.5M حامض الهيدروكلوريك

**عدنان سلطان عبد النبي و لمى طاهر طعمة**

**قسم الكيمياء – كلية التربية – جامعة البصرة**

**الخلاصـــــة**

جرت محاولات عديدة لأستخدم المواد المستخلصة من المواد الطبيعية كمانعات تآكل للعديد من المعادن في عمليات التنظيف بالحامض وذلك لاستبدال بعض المواد الكيمياوية الغالية والسامة والتي تستخدم لهذا الغرض. لذا تم في هذا البحث دراسة الفعل التثبيطي للمستخلص المائي لقشور الرمان على نموذج من الفولاذ الكاربوني في محلول 0.5M من حامض الهيدروكلوريك وباستخدام طريقة الفقدان بالوزن. حيث بينت النتائج بأن هذا المستخلص قادر على إيقاف ذوبان الفولاذ الكاربوني وبمدى واسع يعتمد على تركيز المضاف. كما أكدت حسابات مساحة السطح المغطى (θ) الاستنتاج السابق. وقد بينت النتائج المستحصلة بأن عملية التثبيط تتم من خلال الأمتزاز الفيزيائي للمكونات الكيميائية للمضاف على سطح الفولاذ الكاربوني.