

## Corrosion Inhibition of Carbon steel on Hydrochloric acid Using *Zizyphus Spina – Chritisi* Extract

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### ABSTRACT:

Naturally occurring substances are increasingly being tried to used as corrosion inhibitors of metals in acid cleaning processes to replace some toxic and expensive chemicals currently in use. The corrosion inhibition of carbon steel in hydrochloric acid by *Zizyphus Spina – Chritis* leaves extract was studied using weight loss techniques. Maximum inhibition efficiency and surface coverage were obtained at an optimum concentration. However, an increase in temperature lead to decreased in the inhibition efficiency at the temperature studied. Optimum inhibition efficiency for carbon steel in the presence of *Zizyphus Spina – Chritis* leaves extract was 99.5%, 75% and 66% at 1%,1%and 2% concentration of the inhibitor at 25°C, 35°C and 45°C respectively. The phenomenon of physical adsorption has been proposed from the activation energy values (55.66KJmol<sup>-1</sup>). The surface coverage ( $\theta$ ) 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.

**Key words:** Corrosion Inhibition, Carbon Steel, *Zizyphus Spina – Chritis*, Weight loss method.

### INTRODUCTION:

Carbon steel is employed widely in most industries due to its low cost and availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, ...etc.[1] .According to Vasanth [2] the definition of inhibitor favored by the National Association of Corrosion Engineers (NACE) is; a substance which retards that inhibitors function in one or more ways to control corrosion by adsorption of a thin film onto the surface of a corroding material, by inducing the formation of a thick corrosion product, or by changing the characteristic of the environment resulting in reduced aggressiveness. Acid inhibitors are essentially used in metal finishing industries, acidizing of oil wells, cleaning of boilers and heat exchangers. Naturally occurring substances as inhibition of acid cleaning process has continued to receive attention as replacement for synthesized organic inhibitors. The Investigation into the corrosion inhibition effects of some local plants

[3,4] have proposed parts of economic plants as pickling inhibitors. Not much has actually been achieved using these local plants, compared to the extensive research on synthesized organic inhibitors [5,6].

*Zizyphus Spina – Chritis* is of the Rhamnaceae, it is a genus of about 100 species of deciduous or evergreen trees and shrubs distributed in the tropical and subtropical regions of the world. The *Zizyphus Spina – Chritis* leaves contain different compounds such as, Methyl palmitate , Methyl stearate and Methyl myristate. Beta – sitosterol, Oleanolic acid and Maslinic acid were the main aglycones of the glycosides present in leaves [7].

This study assesses the corrosion inhibition effect of the *Zizyphus Spina – Chritisi* leaves extract on the corrosion of carbon steel in hydrochloric acid medium.

### Experimental:

The tested material was carbon steel type N – 80

of the following composition Table(1).

Table (1): Chemical composition of the material tested N – 80 [8].

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

**Extraction Procedure:**

Fresh leaves of *Zizyphus Spina – Chritis* were dried and ground into powder. 10g was weighed and placed into 100 ml. of (90% methanol) in a 200ml. volumetric flask. The flask was properly corked and left to stand for 48 hours with shaking. The resultant mixture was filtered and the methanol evaporated to

dryness at 65°C using a water bath. A dark brown sticky residue of 0.71g of dried extract [9] was obtained. The dried extract were stored in a refrigerator and a trace of toluene was added to prevent fungal growth until used as a starting material [10].

**Weight loss measurements:**

Weight loss measurements were carried out with metal specimens of carbon steel have dimensions (7.2 x 2.2 x 0.3 cm). All the specimens are vacuum annealed at 500 °C for 5hr. after which they are allowed to cool at room temperature. The specimens are abraded under running tap water using emery paper of 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 [11]. Each coupon was suspended by a glass hook and immersed in 200ml. beakers containing 0.5N HCl solution (Blank) and with additive concentration of 0.5%, 1%, 1.5%, 2%, and 2.5% in 0.5N HCl solution at 25, 35 and 45°C respectively. The specimens weight are measured by electronic balance ( Sartorius BL 210S ) and then suspended into the solution. After 1hr.,3hrs. and 6hrs. in the solution, the specimens were raised from the solution, washed in tap water in order to remove all the corrosion products on 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 following equation [12]:

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

Where:  
 mpy: millis per year.  
 W: is weight loss (mg).  
 D: density (g/cm<sup>3</sup>).  
 A: area of the carbon steel coupon (inch<sup>2</sup>).  
 T: exposure time (hour).  
 The additive percentage inhibition efficiency (%E) was determined from the following equation [13]:

$$\%E = \frac{CR_o - CR_i}{CR_o} \times 100 \dots (2)$$

Where:  
 CR<sub>o</sub> and CR<sub>i</sub> are the corrosion rates in the absence and presence of various concentrations of inhibitor respectively.

**Results and Discussion:**

Visual observation made on carbon steel coupons after 1hr., 3hrs. and 6hrs. immersion in 0.5M HCl solutions containing various concentrations of inhibitor showed that the surface of carbon steel coupons 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. Tables (2,3and 4) and figures(1,2and 3) show the corrosion rate and the inhibitor efficiency for

different inhibitor concentrations at different immersion periods. It was found that as the inhibitor concentration increases, inhibition efficiency will increase suggesting adsorption of the inhibitor material on the metal surface were take place. Maximum inhibition efficiency of about 99.5%, 75% and 66% was reached at 1%,1%and 2% concentration of the inhibitor at 25°C, 35°C and 45°C respectively. It was also found that as the immersion time increased, inhibitor efficiency increased at 25°C, while at 35°C and 45°C it was found decreasing in the inhibitor efficiency as the immersion time increased.

The values of corrosion rate and inhibition efficiency follow similar trend as shown in tables (2,3and 4) and figures(4,5and 6). This minimum corrosion at specific concentration may probably be due to the formation as a soluble complex on metal surface as in the case of polyphosphate or as a result of protonation of additive molecules and subsequent acceleration of the hydrogen evolution process [14]. At higher temperature (45°C) maximum inhibition efficiency was obtained at additives concentration of 2% ,this shift may be due to the adsorption of more inhibitor molecules on the metal surface.

However inhibition decreases with the increase in temperature. The maximum inhibition efficiency is lower at 45°C than at 35°C and 25°C. This is in agreement with what is known about the dependence of adsorption on temperature that as temperature rises, the quantity adsorbed decreases and as a result, the isotherm of higher temperatures is below the isotherm of lower ones. It is of general view that inhibition of metals in acidic solution results from the adsorption of molecules or ions of the inhibitor on the metal surface. The action of organic inhibitor depends on the type of interaction between the substances and the metallic surface. This could cause a change either in the electrochemical process mechanism or on the surface available to the process. The decrease in the inhibition efficiency with increasing temperature suggests weak adsorption interaction between carbon steel surface

$$\text{Log} \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \cdot \frac{1}{T_1} - \frac{1}{T_2} \quad \dots \dots (5)$$

Where:

Ea: Activation energy.

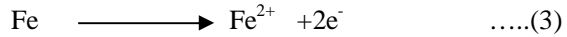
K<sub>2</sub> , K<sub>1</sub> : Corrosion rate at 35 & 45 °C respectively.

R: Gas constant.

T<sub>2</sub> , T<sub>1</sub> : the absolute temperature.

Table(8) reveals that the apparent activation energy, Ea, is higher in the presence of inhibitor than

and the additive, which is physical in nature [15]. Previous studies [16,17] have agreed that the overall reaction of iron dissolution is:



Therefore, the corrosion rate in current density units [18] can be related with the weight loss by equation (4):

$$\text{Icorr. (mA/Cm}^2) = \frac{2 \times 1000 \times W \times F}{A_w \times T \times A} \quad \dots \dots (4)$$

Where:

Icorr. = corrosion current density, (mA/Cm<sup>2</sup>).

F = Faraday constant, 96500 coulombs.

A<sub>w</sub> = Atomic weight of iron, 55.9 .

T = Exposure time, (second).

A = External surface area of the specimen (Cm<sup>2</sup>).

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

Tables (5,6and 7) show the variation of the values of the corrosion current density for the carbon steel specimen in 0.5M HCl solution with the temperature, immersion time and inhibitor concentration. Values of icorr. for the carbon steel in acid solution in the absence of inhibitor are increased with the increasing temperature from 25°C. This is because of the simulating of the anodic reaction with increasing temperature [1,16,19], which leads to increase the diffusion coefficient of oxygen, since the studied system is 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 an increase in the solubility of adsorbed layer which prevents the penetration of H<sup>+</sup> and O<sub>2</sub> to iron substrate.

In order to further support the assertion that physical adsorption is proposed, the values of activation energy (Ea) were calculated using the integrated form of the Arrhenius equation [20]:

in its absence. The experimental results indicate that the energy barrier of corrosion reaction increases as the concentration of inhibitor is increased, since the values of Ea increase with an increase in the concentration of inhibitor. This suggests that the process is activation controlled. The average activation energy value of (55.66KJmol<sup>-1</sup>) for HCl – inhibitor systems (Table – 8) supports the fact that

the inhibitor is physically adsorbed on the carbon steel surface. It follows that the increase in inhibition efficiency is probably due to the increase in the protective multilayer coverage on the entire carbon steel surface. This is in agreement with [21] and reports of Ebenso[22] and Barrow[23]. According to these reports, the activation energy due to chemical adsorption ( $> 80\text{KJmol}^{-1}$ ) is

considerably larger than that due to physical adsorption ( $< 80\text{KJmol}^{-1}$ ). The order of magnitude of the value of average  $E_a$ , indicates a physical mechanism for the adsorption of *Zizyphus Spina – Chritis* leaves extract on to carbon steel surface.

The surface coverage ( $\theta$ ) at each concentration of inhibitor, according to Damaskin[24] was determined using the equation:

$$\theta = 1 - \frac{CR_i}{CR_o} \quad \dots (6)$$

Tables(2,3 and 4) give the calculated values of ( $\theta$ ) at different temperatures, immersion time and inhibitor concentration. At constant temperature,  $\theta$  is increased with increasing inhibitor concentration.

On the other hand, the values of  $\theta$  at a given inhibitor concentration immersion time are decreased with increasing temperature from  $25^\circ\text{C}$  to  $45^\circ\text{C}$ .

The manner in which the values of  $\theta$  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[25]:

$$\frac{C}{\theta} = \frac{1}{b} + C \quad \dots (7)$$

Where b is constant. A plot of C/ $\theta$  values against the corresponding values of C is found to be linear as indicated in figure (7). Hence the mechanism of inhibition may be due to the formation and maintenance of a protective film on the metal surface. The plots further suggest that the additive cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm.

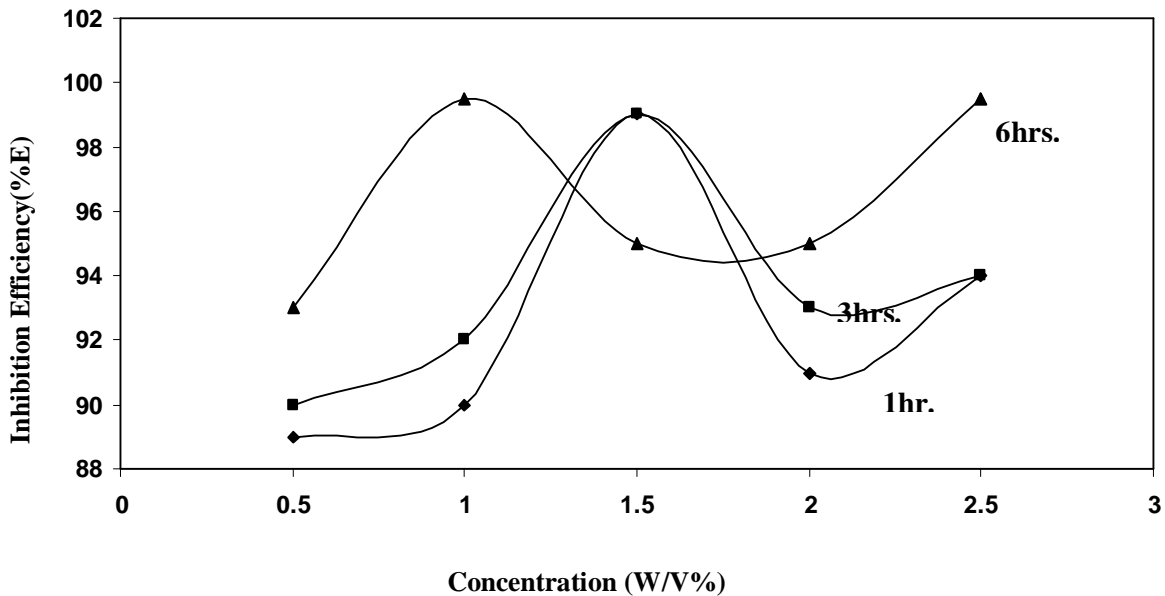


Figure (1): Variation of percentage Inhibition efficiency with various concentration of *Zizyphus Spina – Chritis* leaves extracts for carbon steel coupons in 0.5M HCl solutions at  $25^\circ\text{C}$ .

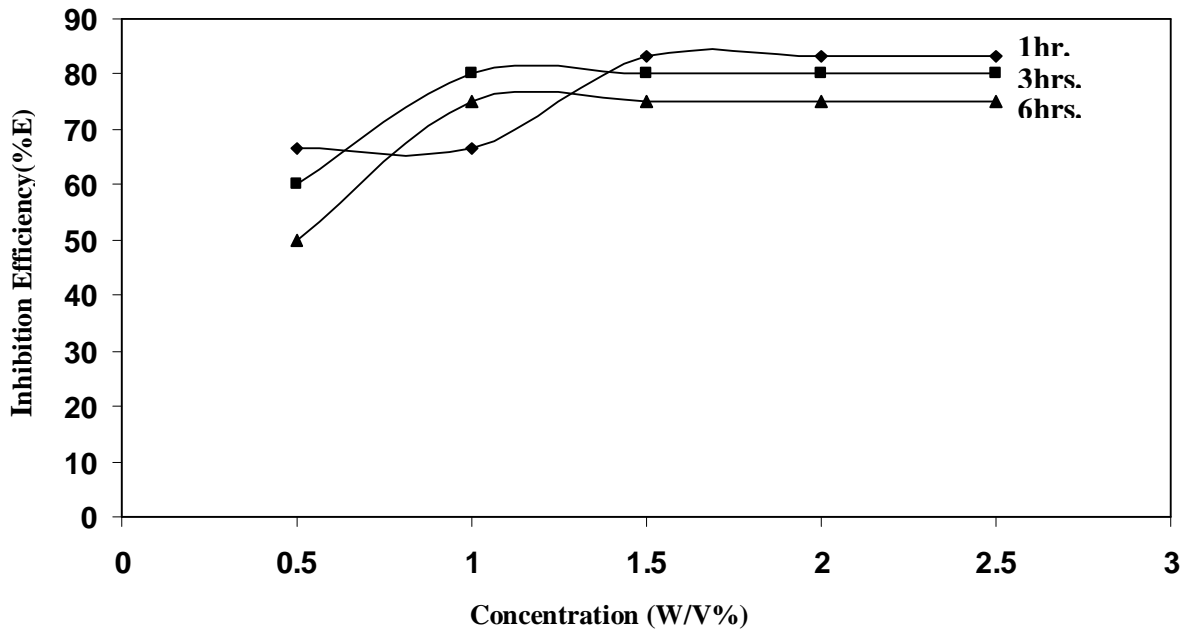


Figure (2): Variation of percentage Inhibition efficiency with various concentration of *Zizyphus Spina - Chrisiti* leaves extracts for carbon steel coupons in 0.5M HCl solutions at 35°C.

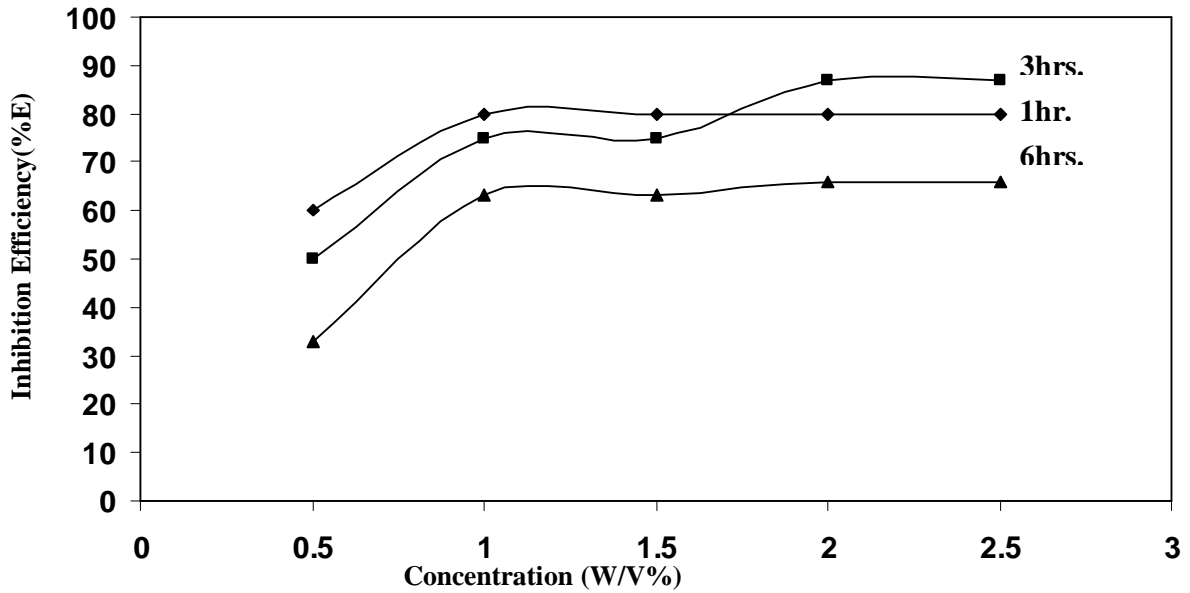


Figure (3): Variation of percentage Inhibition efficiency with various concentration of *Zizyphus Spina - Chrisiti* leaves extracts for carbon steel coupons in 0.5M HCl solutions at 45°C.

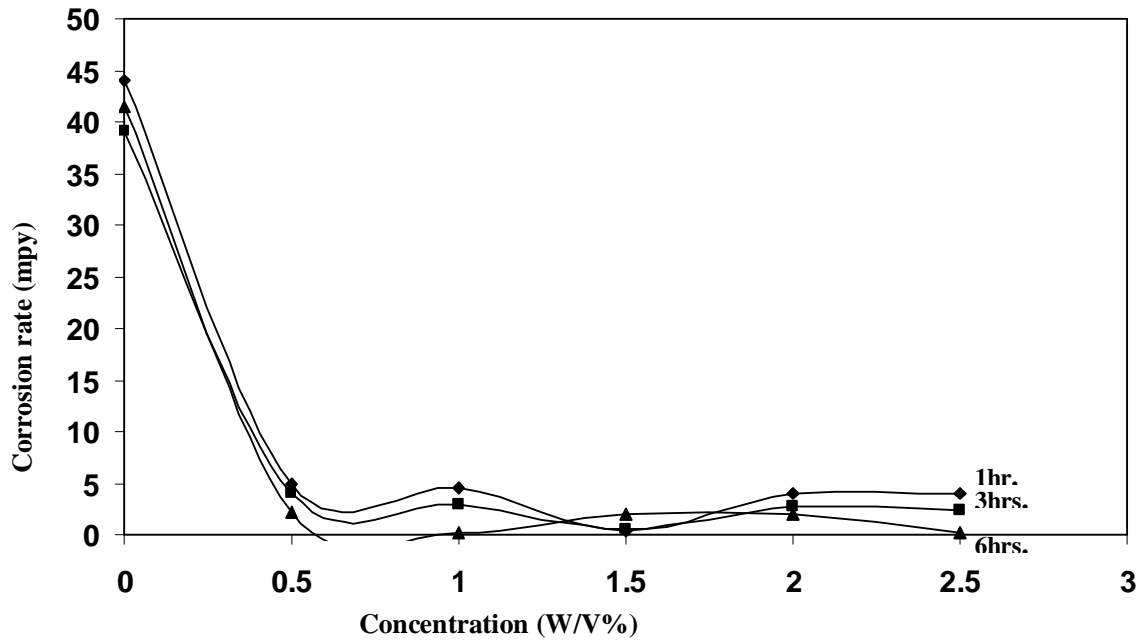


Figure (4): Variation of corrosion rate with various concentration of *Zizyphus Spina - Chrisiti* leaves extracts for carbon steel coupons in 0.5M HCl solutions at 25°C.

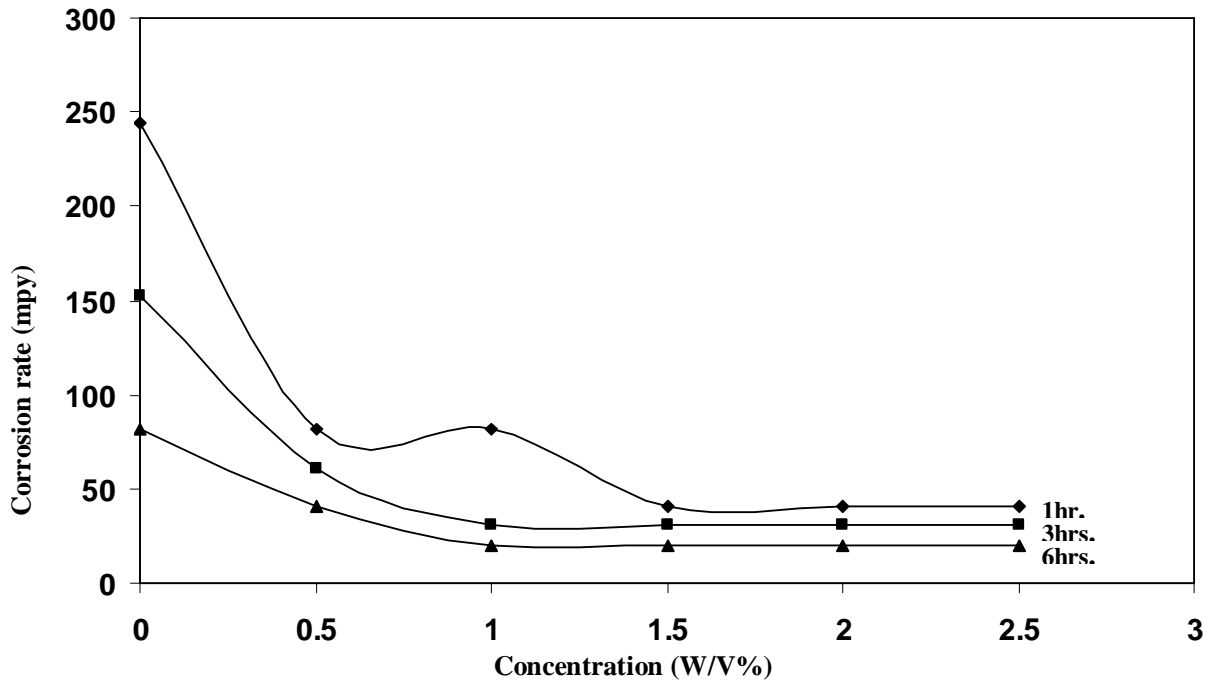


Figure (5): Variation of corrosion rate with various concentration of *Zizyphus Spina - Chrisiti* leaves extracts for carbon steel coupons in 0.5M HCl solutions at 35°C.

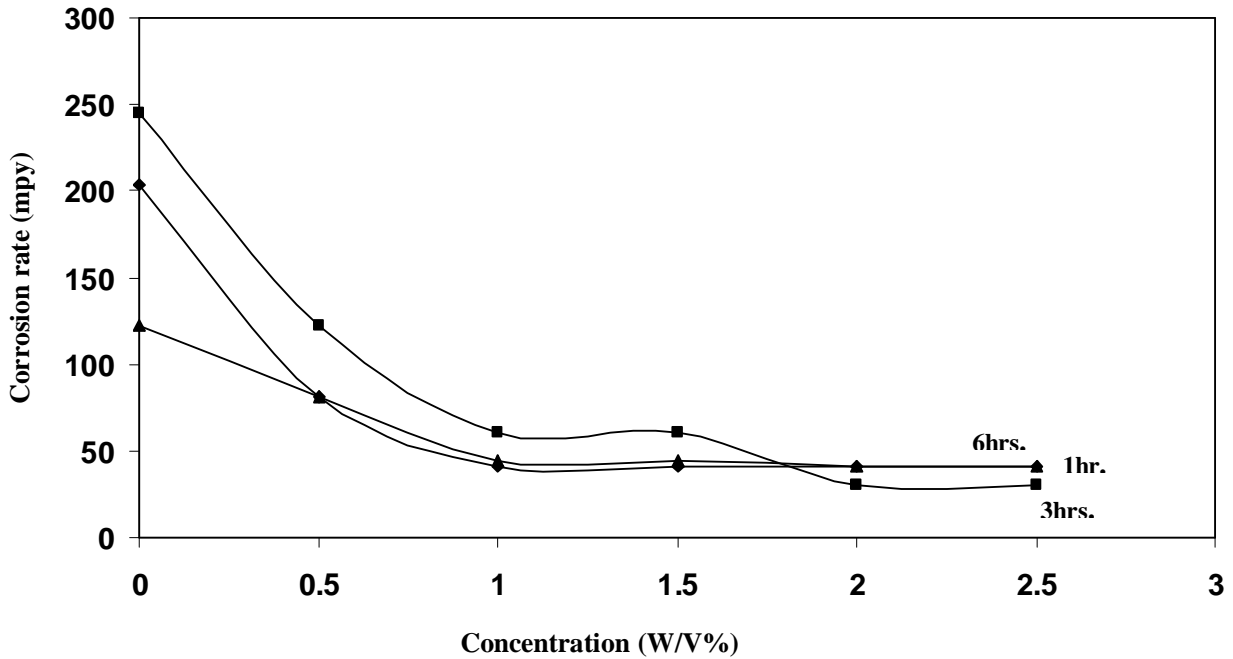


Figure (6): Variation of corrosion rate with various concentration of *Zizyphus Spina – Chrisiti* leaves extracts for carbon steel coupons in 0.5M HCl solutions at 45°C.

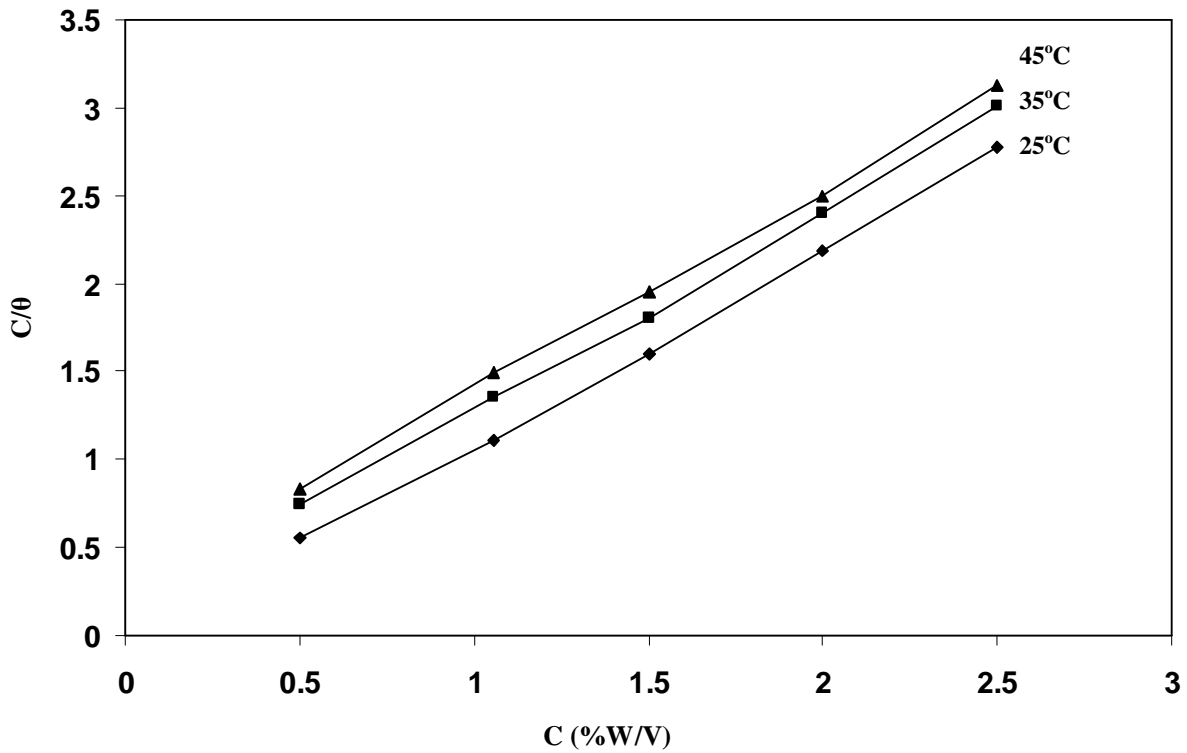


Figure (7): Langmuir adsorption isotherm plotted by  $C/\theta$  versus  $C$  for extract in the carbon steel / 0.5M HCl system at 25°C, 35°C and 45°C.

**Table(2): Percent inhibitor efficiency (%E), corrosion rate (mpy) and Surface Coverage ( $\theta$ ) of carbon steel in 0.5M HCl solution containing various concentration of *Zizyphus Spina Chritis* extract in 25°C at different immersion time.**

Conc.(W/v%)	Time (hours)								
	1			3			6		
	mpy	%E	$\theta$	mpy	%E	$\theta$	mpy	%E	$\theta$
0	44.04	----	----	39.15	---	----	41.50	----	----
0.5	4.89	89	0.89	3.91	90	0.90	2.24	93	0.93
1	4.49	90	0.90	2.94	92	0.92	2.20	99.5	0.99
1.5	0.41	99	0.99	0.49	99	0.99	2.04	95	0.95
2	4.08	91	0.91	2.69	93	0.93	2.04	95	0.95
2.5	4.08	91	0.91	2.45	94	0.94	0.20	99.5	0.99

**Table(3): Percent inhibitor efficiency (%E), corrosion rate (mpy) and Surface Coverage ( $\theta$ ) of carbon steel in 0.5M HCl solution containing various concentration of *Zizyphus Spina - Chritis* extract in 35°C at different immersion time.**

Conc.(W/v%)	Time (hours)								
	1			3			6		
	mpy	%E	$\theta$	mpy	%E	$\theta$	mpy	%E	$\theta$
0	244.68	----	----	152.92	----	----	81.56	----	----
0.5	81.56	66.67	0.66	61.17	60	0.60	40.78	50	0.50
1	81.56	66.67	0.66	30.59	80	0.80	20.39	75	0.75
1.5	40.78	83.33	0.83	30.59	80	0.80	20.39	75	0.75
2	40.78	83.33	0.83	30.59	80	0.80	20.39	75	0.75
2.5	40.78	83.33	0.83	30.59	80	0.80	20.39	75	0.75

**Table(4): Percent inhibitor efficiency (%E), corrosion rate (mpy) and Surface Coverage ( $\theta$ ) of carbon steel in 0.5M HCl solution containing various concentration of *Zizyphus Spina - Chritis* extract in 45°C at different immersion time.**

Conc.(W/v%)	Time (hours)								
	1			3			6		
	mpy	%E	$\theta$	mpy	%E	$\theta$	mpy	%E	$\theta$
0	203.90	----	----	244.68	----	----	122.34	----	----
0.5	81.56	60	0.60	122.34	50	0.50	81.56	33	0.33
1	40.78	80	0.80	61.17	75	0.75	44.39	63	0.63
1.5	40.78	80	0.80	61.17	75	0.75	44.39	63	0.63
2	40.78	80	0.80	30.59	87	0.87	40.78	66	0.66
2.5	40.78	80	0.80	30.59	87	0.87	40.78	66	0.66

**Table ( 5 ): Corrosion current densities (mA/cm<sup>2</sup>) at different immersion time and at different inhibitor concentration of *Zizyphus Spina - Chritis* extract of Carbon steel in 0.5M HCl at 25°C**

Conc.(W/v%)	Corrosion Current I <sub>corr</sub> (mA/cm <sup>2</sup> )		
	1hr.	3hrs.	6hrs.
0	963.67	856.59	910.13
0.5	107.07	85.66	49.08
1	98.15	64.24	4.46
1.5	8.92	10.71	44.61
2	89.23	58.89	44.61
2.5	89.23	53.54	4.46



**Table( 6 ): Corrosion current densities (mA/cm<sup>2</sup>) at different immersion time and at different inhibitor concentration of *Zizyphus Spina – Chritis* extract of Carbon steel in 0.5M HCl at 35°C**

Conc.(W/v%)	Corrosion Current I <sub>corr</sub> (mA/cm <sup>2</sup> )		
	1hr.	3hrs.	6hrs.
0	5353.72	2676.86	1446.14
0.5	1784.57	1070.74	1338.43
1	1784.57	535.37	892.29
1.5	535.37	535.37	892.29
2	535.37	535.37	446.14
2.5	535.37	535.37	446.14

**Table(7): Corrosion current densities (mA/cm<sup>2</sup>) at different immersion time and at different inhibitor concentration of *Zizyphus Spina – Chritis* extract of Carbon steel in 0.5M HCl at 45°C**

Conc.(W/v%)	Corrosion Current I <sub>corr</sub> (mA/cm <sup>2</sup> )		
	1hr.	3hrs.	6hrs.
0	4461.43	4282.97	2676.86
0.5	1784.57	2141.49	1784.57
1	892.29	1070.74	892.29
1.5	892.29	1070.74	892.29
2	892.29	1070.74	446.14
2.5	892.29	1070.74	446.14

**Table(8): Activation Energy (E<sub>a</sub>) of Carbon steel in 0.5M HCl at different immersion time and at different inhibitor concentration of *Zizyphus Spina – Chritis* extract.**

Conc.(W/v%)	Activation Energy (E <sub>a</sub> )KJmol <sup>-1</sup>		
	1hr.	3hrs.	6hrs.
0	14.64	37.77	32.57
0.5	----	55.68	55.68
1	55.68	55.66	55.68
1.5	----	55.66	55.68
2	----	----	----
2.5	----	----	----

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## دراسة الفعل التثبيطي لمستخلص أوراق السدر على الفولاذ الكربوني في حامض الهيدروكلوريك

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### الخلاصة

جرت محاولات عديدة لأستخدام المواد المستخلصة من المواد الطبيعية كمانعات تأكل للعديد من المعادن في عمليات التنظيف بالحامض وذلك لاستبدال بعض المواد الكيماوية الغالية والسامة والتي تستخدم لهذا الغرض. لذا تم في هذا البحث دراسة استخدام مستخلص أوراق السدر في تثبيط تأكل الفولاذ الكربوني في محلول 0.5M من حامض الهيدروكلوريك وباستخدام طريقة الفقدان بالوزن. تم تحديد أقصى كفاءة تثبيط واكبر جزء من المعدن مغطى بالمتببط حيث بلغت أقصى كفاءة تثبيط 99.5% و 75% و 66% وذلك عند تراكيز من المتببط 1% و 1% و 2% وعند درجات حرارة 25م و 35م و 45م على التوالي. حيث بينت النتائج بأن هذا المستخلص قادر على إيقاف نوبان الفولاذ الكربوني وبمدى واسع يعتمد على تركيز المضاف وكذلك زمن التعرض للحامض.. كما أكدت حسابات مساحة السطح المغطى ( $\theta$ ) الاستنتاج السابق. وقد بينت النتائج المستحصلة بأن عملية التثبيط تتم من خلال الأمتزاز الفيزيائي للمكونات الكيمائية للمضاف على سطح الفولاذ الكربوني.