

Citrullus colocynthis Extract as Corrosion inhibitor for carbon low steel in Acid Medium using Weight Loss Method

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Abstract

corrosion inhibition of carbon low steel using methanol extract of the fruits of *Citrullus colocynthis* was studied using weight loss measurement at 303,323 and 333°K. The inhibition efficiency increased with the increase in inhibitor concentration but decreased with temperature. The Langmuir adsorption isotherm was tested for their fit to the experimental data . The apparent activation energies ,entropies of the dissolution process and the free energies for the adsorption process were determined and discussed .All computed quantum chemical parameters are found to correlate well with experimental inhibition efficiency of inhibitor.

Keyword: Corrosion inhibition, Carbon low steel, Acid medium, kinetics, and thermodynamics

مستخلص الحنظل كمثبط لتآكل الفولاذ منخفض الكربون في الوسط الحامضي باستخدام طريقة فقدان الوزن.

الخلاصة

تمت دراسة تثبيط التآكل لفولاذ منخفض الكربون باستخدام مستخلص الميثانول لثمار الحنظل باستخدام طريقة فقدان الوزن وفي ٣٠٣، ٣٢٣ و ٣٣٣ كلفن . كفاءة التثبيط تزداد مع زيادة تركيز المثبط ولكنها تتخفض مع الحرارة. أن امتزاز الجزيئات على سطح المعدن يخضع لمعادلة امتزاز لانكماير . تم تعيين قيم الثوابت الترموديناميكية ،طاقة التنشيط ، حرارة التفاعل و العشوائية لعملية ذوبان المعدن وتم كذلك تعيين الطاقة الحرة لعملية الامتزاز، وتم مناقشة هذه النتائج. ووجد هناك تناسب كبير بين قيم عملية كفاءة التثبيط والقيم المحسوبة من كيمياء الكم .

1. Introduction

The use of inhibitors is one of the most practical methods for protecting against corrosion, especially in acid descaling bathes, to prevent not only metal dissolution but also acid consumption (1) . inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the film formed on the metal surface (2). It has been observed that the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and π orbital character of donating electrons and also on the electronic structure of the inhibitor (3) .It has been accepted that the corrosion inhibition process results from the formation of an organic inhibitor film on the metal surface by the compounds containing heteroatoms like N, O, S, and hence thioureas have proved to be fairly effective in corrosion control (4-5) Recently, many research studies have been focused on natural extracts that can replace synthetic compounds (6-7) .Extracts of various plants have been investigated for use as inhibitors such as *Nyctanthes arbortristis*(8) ,*Nerium oleander* and

Tecomastans (9) , *Indian Gooseberry Oxandra asbeckii* (10) ,*ginkgo* (11) ,*Stevia rebaudiana* (12) ,*Sesbania sesban* (13) ,*Lupinus varius l.* (14) ,*Dodonaea viscosa* (15) , *Annona squamosa* (16) , *Black Pepper* (17) ,*Moringaoleifera* (18) ,*Pterocarpussoyauxi* (19) ,*green tea* (20).Therefore the objective of the present study is aim to investigate inhibitive and adsorption properties of alcoholic extract of *Citrullus colocynthis* fruits for the corrosion of carbon low steel in H₂SO₄

2. Material and Method

2.1 Sample collection

fruits of *Citrullus colocynthis* were collected from Nasiriyah city at Iraq. Fruits were cleaned , washed by distilled water, dried at room temperature for one day , ground as powder and kept in dark glass containers for further use.

2.2 Preparation of plant extract

(50 g) of the dry fruits powder were placed in 500ml round bottomed flask containing 250ml methanol (100%) and refluxed for 1h in boiling degree.After that the mixture was filtered in Buchner funnel by Whatman no.1 filter paper by the aid of vacuum pump. The filtrate was then used for chemical

analysis(Test for Flavonoids , Alkaloids and Saponins)
The filtrate solution was evaporated through rotary evaporator under reduced pressure at 40°C until drying and then weighted and kept for further use .

2.3 Weight Loss Tests

1- specimens of carbon low steel used in this study has the following Chemical composition (wt%): C(0.20) , Si(0.24) Ni(0.15) ,Cu(0.18) ,Cr(0.10) ,Mn(0.44) , S(0.05) ,P(0.05) and (98.25). The weight loss tests were performed on metallic samples of carbon low steel with dimensions of 2.83cm ×0.32cm .

2-The specimens were polished mechanically using SiC emery papers of grade 220, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and acetone and stored in moisture free desiccators before their use in corrosion studies.

3-Polished specimens were initially weighed in an electronic balance.

4- Weighed samples are immersed in the test solution without and with different concentrations of the inhibitor for various intervals of time.

5- At the end of the tests, the specimens were carefully washed in absolute ethanol having used nitric acid to quench further corrosion from taking place, and then reweighed⁽²¹⁻²²⁻²³⁾.

The experiments were performed for various parameters such as:-

- Concentration of the inhibitor (0.025, 0.05, 0.075 g/l).
- Temperature variation (303, 323, 333 °K).
- Different the corrosive medium (H₂SO₄)
- Different immersion time (2, 4, 8, 24 hours).

Corrosion Rate: From the change in weight of specimens the corrosion rate was calculated using the following relationship⁽²⁴⁾

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

W : weight loss in milligram

D: density of specimen g/cm³

A: area of specimen in square inch (noting that 1 in² = 6.5416 cm².)

T : exposure time in hours

mpy = mils per year (1mil =1inch /1000)

3. Results and Discussion

3.1: Qualitative Tests of Some Active Compounds in Plant Extract

Table(3-1) shows the results obtained from phytochemical analysis performed on Citrullus colocynthis. These compounds contain oxygen and nitrogen atoms which are the centre of adsorption. The Citrullus colocynthis extract establish their inhibitive action through adsorption of phytochemical component

molecules on the metal surface. The results of phytochemical screening is shown in Table (3-2).This result was found to be in agreement with the findings of (V. Prasanth et al., 2012, Abdelrahim A.et al ., 2013, Sandhya V. and S.D. Biradar.,2013)(25-26-27)

Table 3-1:Phytochemical screening of fruit extract of Citrullus colocynthis

Reagent	Component	Result
Alcohol Potassium hydroxide	Flavonoids	+
Wagner	Alkaloids	+
HgCl ₂	Saponins	+

Fig. 1 show the variation of weight loss with time for the corrosion of carbon low steel in 1 M H₂SO₄ (at 303 °K) containing various concentration of methanol extract of fruits of Citrullus colocynthis . The figures revealed that the weight loss of carbon low steel in 1 M H₂SO₄ increases with increase in the time of contact , but decreases with increase in the time of concentration of methanol extract of the fruits of Citrullus colocynthis, indicating that the extract inhibit the corrosion of carbon low steel in H₂SO₄ .At 323 °K and 333 °K , the values obtained for weight loss were relatively higher than the values obtained at 303 °K,indicating that the rate of corrosion of carbon low steel in H₂SO₄ increased with increase in temperature.

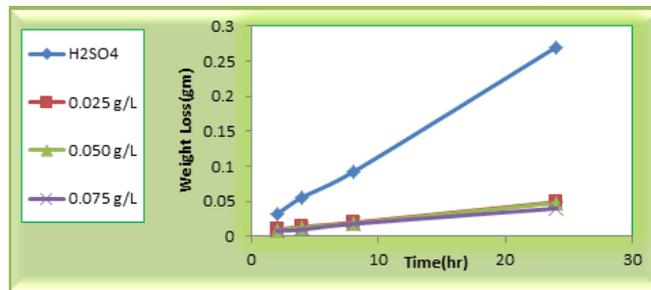


Figure1: Variation of weight loss of carbon low steel with time for the corrosion of carbon low steel in H₂SO₄ containing various concentration of methanol extract of Citrullus colocynthis fruits at 303 °K

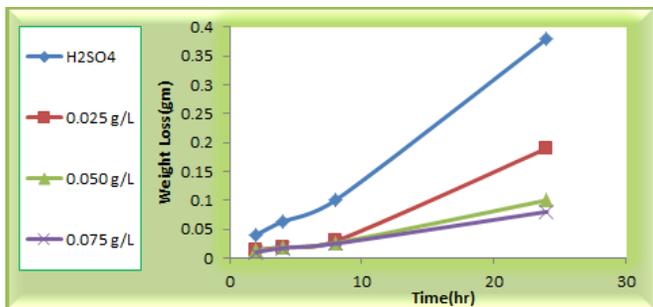


Figure2: Variation of weight loss of carbon low steel with time for the corrosion of carbon low steel in H₂SO₄ containing various concentration of methanol extract of Citrullus colocyntis fruits at 323 °K

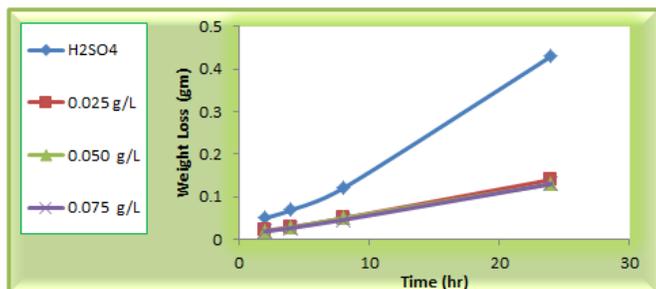


Figure3: Variation of weight loss of carbon low steel with time for the corrosion of carbon low steel in H₂SO₄ containing various concentration of methanol extract of Citrullus colocyntis fruits at 333 °K

Values of the corrosion rates of carbon low steel (in the absence and presence of methanol extract of fruits of Citrullus colocyntis is recorded in Table 3-2.

Table 3-2: Corrosion rates of carbon low steel and inhibition efficiencies of methanol extract of Citrullus colocyntis fruits at 24hr

Con (g/L)	CR(mpy)			%IE		
	303 °K	323 °K	333 °K	303 °K	323 °K	333 °K
H ₂ SO ₄	333.12	459.76	531.90			
0.025	60.432	131.45	172.56	82.31	72.26	67.63
0.050	58.078	127.72	168.03	82.56	72.57	67.72
0.075	55.009	99.309	163.00	83.02	78.01	68.00

Results shown in the table 3-2 revealed that corrosion rates increase with increasing temperature. This due to the desorption aided by increasing the temperature, this behavior reveals is physical adsorption (28), the highest values (531.90 mpy) obtained at 333 °K both in the absence and presence of the extract. The lowest value of the corrosion rate was observed to be 55.009 mpy at 303 °K in the presence of the extract.

From Table 3-2 it is seen that inhibition efficiency of extract decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption mechanism. A similar conclusion has been reached by (L. A. Nnanna et al., 2011, N S Patel et al., 2013, A. J. Abdul Nasser et al., 2012) (29-30-31). The percentage inhibition efficiency (IE%) was observed to increase with the addition of methanol extract of fruits of Citrullus colocyntis concentration and reaches maximum at an optimum concentration of extract (0.075 g/L) for all immersion time periods. The maximum (IE%) (83.02%) was observed at 0.075 g/L of methanol extract of fruits of Citrullus colocyntis for 24hr exposure time at 303 °K. This behavior can be attributed to the increase of the surface area covered by the adsorbed molecules of methanol extract of fruits of Citrullus colocyntis. Components of extract such as (Flavonoids, Alkaloids and Saponins) adsorbed over the carbon low steel surface blocking the active sites in which direct acid attacks proceed and protect the metal from corrosion. Some of these components have heteroatoms such as N and O in their molecules (32-33). Thus, the corrosion of carbon low steel may be attributed to the adsorption of Citrullus colocyntis extract components through these atoms, which are regarded as centers of adsorption onto the metal surface thereby creating a barrier for mass and charge transfer and thus isolates the metal from further attack of the corrosive anions (34).

3.2 Kinetic parameters

Thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS) of activation of corrosion process may be evaluated from the effect of temperature. The enthalpy and entropy of activation of corrosion process was calculated from the equation:

$$R_{corr} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \dots\dots\dots(2)$$

where h is Planck's constant, N is the Avogadro's number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation. Fig. 4 represent the relation between log R_{corr} vs. 1/T for metals in 1M H₂SO₄ in the absence and presence (0.025 g/L, 0.050 g/L, 0.075 g/L) of the studied inhibitor. Inspection of Table 3-3 reveal that, the activation energy increases in presence of the inhibitor and consequently the rate of corrosion reaction is decreased. Thus the activation energy values support the fact that the inhibitor was physically adsorbed on the metal surface in all media. The activation energies were also observed to increase with increasing in the concentration of the extract, indicating that there is

increasing ease of adsorption of the inhibitors with increasing concentration. This is in accordance with the findings of(Nawafleh E.et al.,2012, Deepa Prabhu and Rao Padmalatha.,2013, Omya R. and Shadia M.,2011.) (35-36-37) It has been reported that when the values of $E_a > 80$ kJ/mol it indicates chemical adsorption whereas $E_a < 80$ kJ/mol infers physical adsorption(38-39). In the present study, a physical adsorption mechanism is proposed since the values for the E_a are less than 80 kJ/mol .

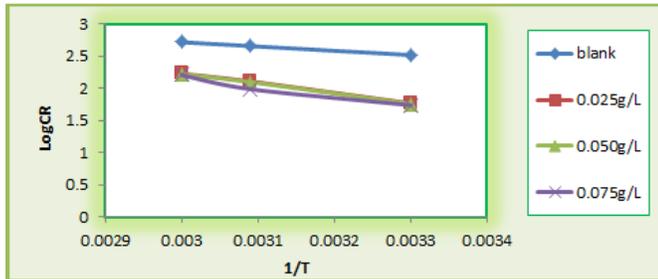


Figure 4: Log (corrosion rate (mpy)) - 1/T curves for carbon low steel dissolution in 1M H₂SO₄ in the absence and presence of extract

Fig.5 represent the relation between log (R_{Corr} / T) vs. 1/ T for metal in 1M H₂SO₄ in absence and presence of various concentrations the inhibitor. Straight lines were obtained with slope equal to($-\Delta H^* / 2.303 RT$) and an intercept of $\log[(R/Nh) + (\Delta S^*/2.303R)]$.The calculated values of the apparent activation enthalpies ΔH^* and activation entropies, ΔS^* are given in Table 3-3.Enthalpy of activation of absolute values lower than 41.86kJmol⁻¹ indicates physical adsorption, and values approaching 100 kJmol⁻¹ indicate chemical adsorption (40) . In this study, the values of ΔH^* are lower than 41.86 kJmol⁻¹ confirming physical adsorption. The positive signs of ΔH^* reflect the endothermic nature of the metal corrosion process(37-41-42). The values of the entropy change of activation (ΔS^*) in the absence and presence of the extract is large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step. This means that the activated molecules were in higher order state than that at the initial state(43) .

Table 3-3 Thermodynamics and activation parameters for carbon low steel in presence of extract

Con.(g/L)	$\Delta H(KJ mol^{-1})$	$E_a(KJ mol^{-1})$	$\Delta S(KJ mol^{-1} K^{-1})$
H ₂ SO ₄	10.45	13.14	-0.1925
0.025	29.20	31.89	-0.2005
0.050	29.49	32.18	-0.2007
0.075	21.39	24.08	-0.2035

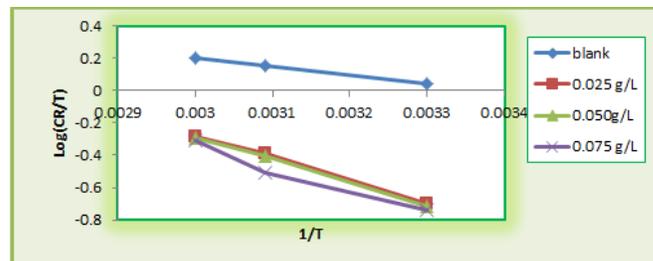


Figure5: Log (corrosion rate (mpy)/T) - 1/T curves for carbon low steel dissolution in 1M H₂SO₄ in the absence and presence of extract

3.3 Adsorption isotherms

In order to obtain the adsorption isotherm, The θ value for inhibitor concentration at different temperatures has been calculated according to equation (3) The experimental results were best fit with Langmuir adsorption isotherm ⁽⁴⁴⁾, The Langmuir adsorption isotherm is given by Eq. (3), ⁽³⁸⁻³⁹⁾

$$C/\theta = (1/K) + C \dots\dots\dots(3)$$

where C: is the inhibitor concentration
 θ : is the degree of surface coverage of the inhibitor

K_{ads} . is the equilibrium constant of the adsorption process.

The K value is related to the Gibbs free energy of adsorption, ΔG°_{ads} , according to the following equation ⁽⁴⁵⁾:

$$K_{ads} = (1/ 55.5) \exp - \Delta G^{\circ}_{ads} / RT \dots\dots\dots(4)$$

where 55.5 is the molar concentration of water in the bulk solution in mol L⁻¹, R is the universal gas constant and T is the absolute temperature.As shown in Fig.6 the plot of C/θ versus C for metal in the corrosive medium with different inhibitor concentrations, yields a straight line showing that the adsorption of the inhibitor is well described by the Langmuir isotherm. The calculated values of k and ΔG° of the adsorption reaction of metal are shown in Table 3-4.The extract of *Citrullus colocynthis* contain the phytochemical constituents such as alkaloids, saponin and flavonoids compounds. The phytochemical constituents present in *Citrullus colocynthis*, having many active centers such as oxygen and nitrogen, are adsorbed on the metal surface and the effectiveness of these inhibitors on the corrosion of carbon low steel may be due to the electron densities on the active centres. Generally, the values of ΔG°_{ads} around -20kJ/mol or lower are consistent with physisorption, while those around -40kJ/mol or higher involve chemisorptions ⁽⁴⁶⁻⁴⁷⁻⁴⁸⁾The result is presented in Table 3-4. The values ΔG_{ads} are negative and less than -40 kJmol⁻¹. This implies that the adsorption of the inhibitor on metale surface is spontaneous and confirms

physical adsorption mechanism(49-50-51) . The positive values of adsorption equilibrium constant K_{ads} imply a better adsorption, which leads to an increase in the inhibition efficiency (52)The adsorption equilibrium constant K_{ads} decreases with increase in experimental temperature[Table 3-4] indicating that the interactions between the adsorbed molecules and the metal surface are weakens and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature(53-54)

Table 3-4 Adsorption parameters from Langmuir isotherm for extract and 1M H₂SO₄ for metal corrosion at 303 ,323 and 333 °K

T (°K)	$K_{ads}(\text{mol}^{-1})$	$\Delta G_{ads}(\text{KJ/mol})$
303	65.21	-20.64
323	47.29	-21.14
333	28.33	-20.14

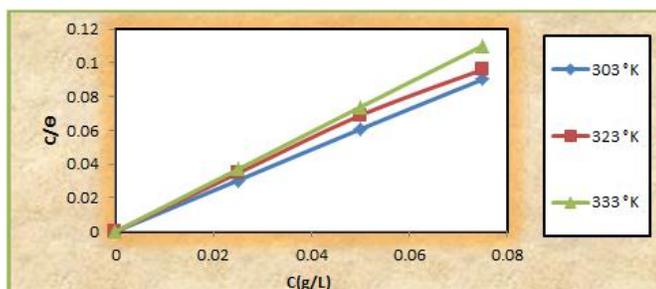


Figure 6: Langmuir adsorption plots for carbon low steel in 1M H₂SO₄ at different temperatures in presence of various concentration of extract

Conclusions

The following conclusions can be drawn from this study:

- 1- The *Citrullus colocynthis* extract were found to be an efficient natural corrosion inhibitor for carbon low steel in 1M H₂SO₄ solutions by using weight loss techniques.
- 2-The % IE increased with the increase in inhibitor concentration and decrease with rising the temperature at all concentrations.
- 3- The % IE increased with the increase in immersion time of the metals in 1M H₂SO₄
- 4-The corrosion rates were observed to decrease with increase in concentration of *Citrullus colocynthis* extract but increase with temperature.

5- The weight loss of metal in 1M H₂SO₄ decreases with the inhibitor concentration increases.

6-The inhibitive effect of *Citrullus colocynthis* extract are ascribed to the presence of organic compounds in the extract.

7-The negative values of ΔG indicate that the adsorption of the inhibitors on the metal surface is spontaneous. E_a and ΔH values of the corrosion process also support this observation.8- All values of ΔS^*_{ads} are negative for the blank and inhibited solution which implies that the activation complex in the rate determining step represents association rather than dissociation step.

9.The adsorption characteristics of *Citrullus colocynthis* extract on the metal surface were approximated by Langmuir adsorption isotherm, and it obeyed and fitted this model.

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