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Effect of Pomegranate shells extract as natural Corrosion the inhibitor for C-Steel by using electrochemical technique

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Abstract

This study involves the efficiency evaluation of pomegranate shells extract as natural corrosion inhibitor for C-Steel in 1N HCL at various temperatures (293,323and343) °K using electrochemical technique. The results show that the inhibition efficiency increases with increasing the extract concentration and decreases with increasing temperature. The results of Potentiodynamic polarization curves indicate that the pomegranate shells extract behaves as a mixed type inhibitor. The thermodynamic functions of dissolution and adsorption processes were determined from experimental polarization curves and the interpretation of the results is given. The apparent activation energy, enthalpy , entropy and free energy of the dissolution process were determined and discussed.The Surface analysis (SEM and FT-IR) was also carried out to establish the corrosion inhibitive property of the pomegranate shells extract in 1N HCL. Metallurgical Microscope and FT-IR tests indicated that the pomegranate shells extract had high efficiency on adsorption on C-Steel from through function groups (carbonyl, phenol and amines). The results obtained showed that the pomegranate shells extract could serve as an effective natural inhibitor for the corrosion of C-Steel.

Key words: Natural corrosion inhibitors, Pomegranet extracts, Thermodynamics of corrosion inhibition, Potetiodynamic curves.

Introduction

The use of organic inhibitors is one of the most practical methods for protecting metals against corrosion especially in acidic media [1-4] which is commonly used in the cleaning process of metal surfaces.

The efficiency of the organic compounds as corrosion inhibitors is closely associated with their chemical adsorption characteristics [5]. Most organic compounds contain: nitrogen, sulfur, oxygen, and unsaturated bonds in their structure, through which they can be adsorbed onto the metal surfaces [6]. Some authors describe this interaction as a chelating reaction between the metal surface and the organic compound [7]. Several classes of organic compounds show good anticorrosive efficiency mainly amino, hydroxyl phenols, aromatic carboxylic acids and sulphure compounds. On the other hand, most of the amines are highly toxic and most aromatic amines are carcinogenic. These inhibitors may cause temporary or permanent damage to organ system such as kidneys or liver, or to disturb the biochemical process and the enzymatic system in the human body [8].

The toxicity may manifest either during the production of the inhibitors or during their applications. These features of amine compound lead to focus and investigate the use of naturally occurring substances as corrosion inhibitor.Recently, plant extracts became an important environmentally friendly, renewable source for a wide range of inhibitors. Plant extracts are viewed as an incredibly rich source of naturally occuring compounds that can be extracted by simple procedures with low cost. Various natural products have been evaluated and some of them are currently used as corrosion inhibitors for different applications

[9-14]. Acids such as HCl and its aminosalts are widely used as pickling, de scaling and cleaning agents in several industries for the removal of undesirable oxide films and corrosion products [15]. In many industries, mild steel (MS) is the material of choice in the fabrication of reaction vessels, storage tanks etc., which is easily subjected to corrosion in the presence of acids [16].

In the present study, the corrosion inhibition properties of pomegranate fruit shells extracts in 1 N HCl were investigated by electrochemical method for C-Steel.

E xperimental

Preparation of pomegranate shells extract

Pomegranate fruit shells were dried, grounded to fine powder. The powder was extracted with boiling water using Soxhlet apparatus. The extract was evaporated to obtain the solid water soluble residue, which was used as corrosion inhibitor. The solid extract was used to study the corrosion inhibition properties at various concentrations of the pomegranate inhibitor and at three different temperatures.

Chemical test

a-pomegranate shells extracts gave positive indication for alkaloid test.

b - pomegranate shells extracts gave positive result with phenol test.

The chemical composition of pomegranate shells has been investigated and reported elsewhere as being rich with polyhydroxy phenols, flavinoids and alkaloids.[17]

Specimen preparation

C-Steel specimens having the following composition: C= 0.07%, Mn= 0.34%, P= 0.08% and remaining % Fe, were used in the present study. C-Steel cylindrical specimen coupons ;1 cm^2 cross section area were used in the Electro chemical measurements and SEM analysis .The exposed area was mechanically polished with (220,400,800 and 1000) grades of emery papers ,then cleaned with deionized water and degreased with ethanol and acetone then dried in vacuum desiccators at room temperature before being used in the electrochemical experiments

Instrumentation

The electrochemical measurements were carried out using WENKING M lab, Perkin Elemer company, Baghdad University. The experiments were performed in a conventional three electrodes cell consisting of a steel working electrode (WE), platinum counter electrode (CE) and a saturated calomel reference electrode (SCE).

Solution preparation

(1N HCl) 35% solutions were prepared containing three different concentrations from the pomegranate shells extracts, (1,5 and 10 ppm).

Results and Discussion

Polarization measurements

The polarization behavior of C- steel under standared conditions (control experiment), and in the presence of three concentrations of pomegranate shells extracts (1,5 and 10 ppm) was investigated at three temperatures (293,323,and 343) K. The obtained curves are shown in Figs. (1-12).The corrosion parameters determined from the curves: Ecorr, Icorr, Tafel slope constants (βa ,β_c), liner polarization resistance(Rp) are presented in Table (1). The current density (Icorr) was obtained by the extrapolation of the Tafel lines. The display data showed that increasing the pomegranate extract concentration decreases the corrosion current density (Icorr) and consequently the corrosion rate(W) [18,19]. This confirms the inhibition action of pomegranate shells extract on protecting the metal surface. The change of the corrosion rate with the temperature was studied in the presence of extracts. Generally the corrosion rate increases with the rise of temperature [20-23]. The corrosion rate was found to increase with temperature, but the change in the corrosion rate was much lower in the presence of the pomegranate shells extract than the controlled experiments. (see Table 2).

The protection efficiency (%IE) was calculated from the electrochemical relation as: [21].

$$\text{Inhibitors Efficiency (IE\%)} = \frac{W_{uninh} - W_{inh}}{W_{uninh}} \times 100 \qquad (1)$$

Where W_{inh} and W_{uninh} are the corrosion rate of the C-Steel coupons in presence and absence of inhibitor, respectively .The obtained data are listed in the Table (1). The obtained data showed that the inhibition efficiency increased with increasing concentration of the inhibitor but decreased with increasing temperature. The inhibition efficiency of the extract is due to the adsorption of the alkaloid and poly hydroxyl phenols constituent of the extract on the metal .Similar trend was observed with cafenic acid extract [24]. The high inhibition efficiency obtained at these low concentrations suggests that the pomegranate shell extract could serve as effective corrosion inhibitor and food antioxidant additive.

The observed Ecorr values did not shift to any practical direction from the blank values, which indicates that the inhibitor acts through mixed mode of inhibition. The addition of pomegranate shells extract affects both anodic and cathodic parts of the polarization curves, indicating that it can be classified as a mixed type inhibitor. The corrosion current density was calculated from the intersection of cathodic and anodic tafel lines. The slight variations in anodic and cathodic tafel slopes (βa ,β_c)indicate that the inhibiting action is taking place simply by blocking the cathodic and anodic sites on the metal surface. The increase in linear polarization resistance (Rp) values with the increase in the concentration of inhibitor indicates the inhibitor efficiency as natural inhibitor and food additive antioxidant.

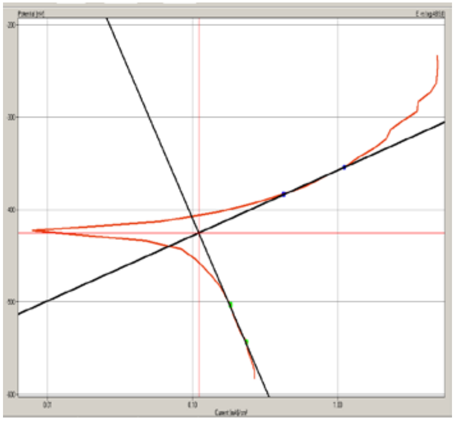


Fig. 1. Polarization curves for C- steel 1N HCL at 293 k^o .

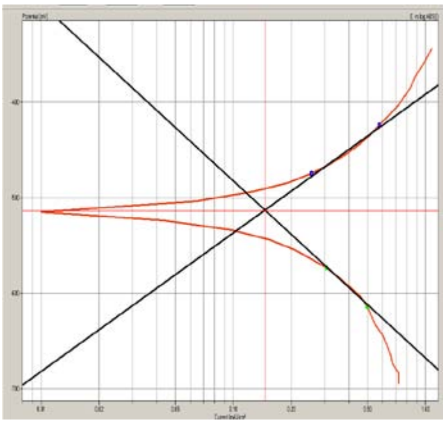


Fig. 2. Polarization curves for C- steel in in 1N HCl at 323 k^o .

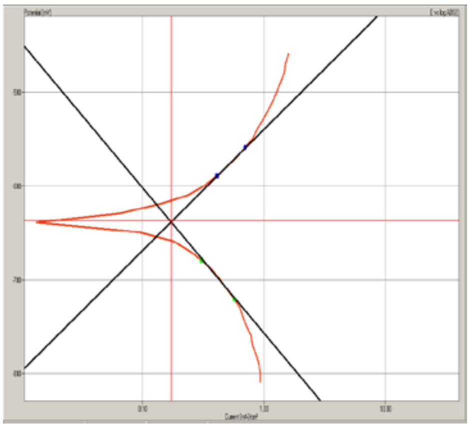


Fig. 3. Polarization curves for C- steel in 1N HCl at 343 k^o **.**

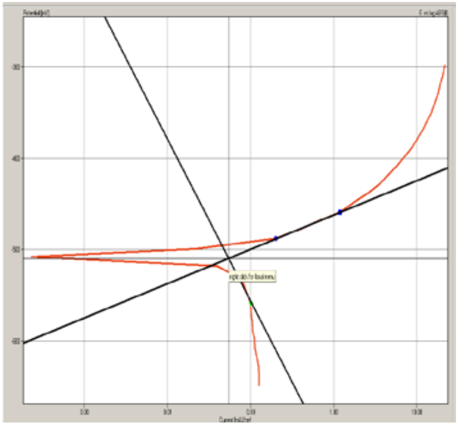


Fig. 4. Polarization curves for C- steel in 1N HCl containing 1 ppm pomegranate shells extracts at 293 k^o .

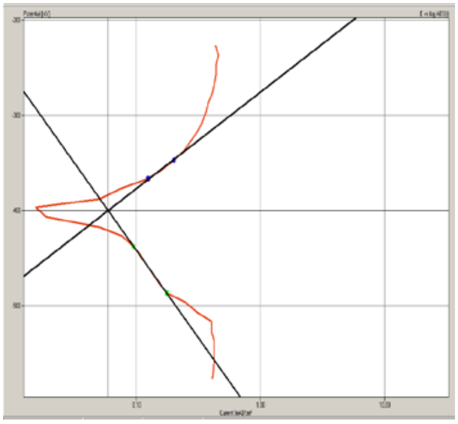


Fig. 5. Polarization curves for C- steel in 1N HCl containing 1 ppm pomegranate shells extracts at 323 k^o .

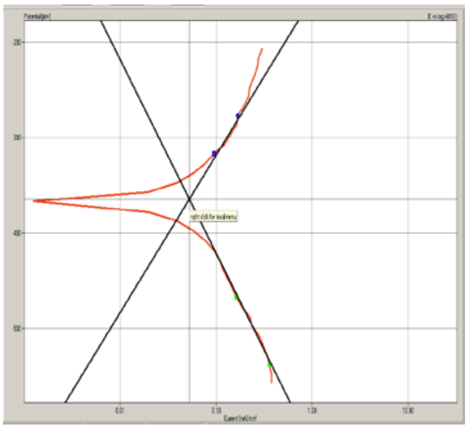


Fig. 6. Polarization curves for C- steel in 1N HCl containing 1 ppm pomegranate shells extracts at 343 k^o .

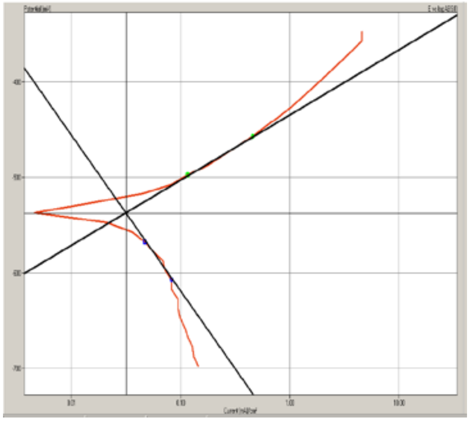


Fig. 7. Polarization curves for C- steel in 1N HCl containing 5 ppm pomegranate shells extract at 293 k^{o} .

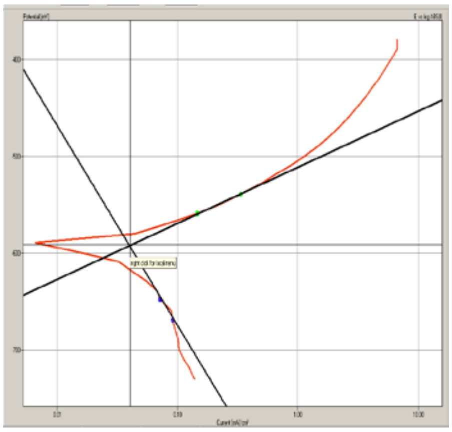


Fig. 8. Polarization curves for C- steel in 1N HCl containing 5 ppm pomegranate shells extracts at 323 k^{o}.

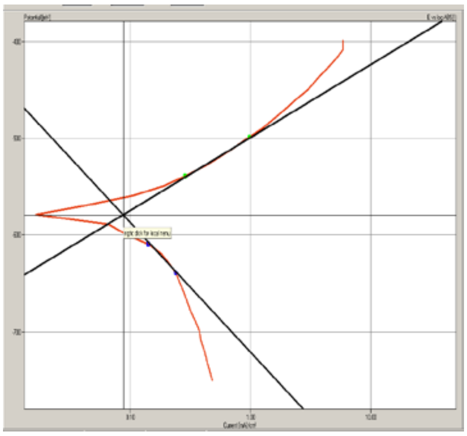


Fig. 9. Polarization curves for C- steel in containing 5 ppm pomegranate shells extracts at 343 k^{o} .

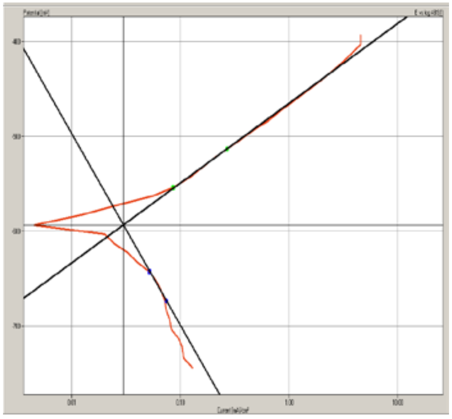


Fig. 10. Polarization curves for C-Steel 1N HCl 1N HCL containin10 ppm pomegranate shells extracts at 293 k^{o} .

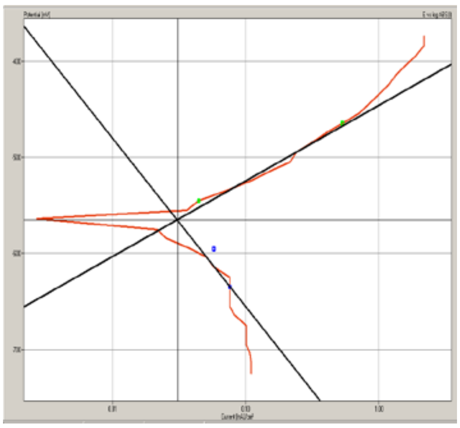


Fig. 11. Polarization curves for C-Steel in containing 10 ppm pomegranate shells extracts at 323 k^{o} .

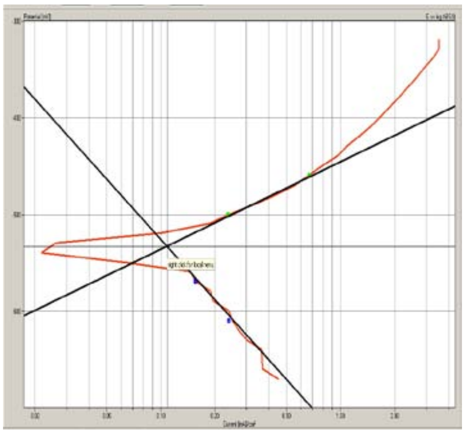


Fig. 12. Polarization curves for C- steel in 1N HCL 1N HCL containing 10 ppm pomegranate shells extracts at 343 k^{o}.

Table 1 : Electrochemical parameters of C-Steel

Comp.	conc. ppm	Temp. K°	βa Mv/dec	-βc Mv/dec	Rp Ω/cm2	-Ecorr Mv	Icorr mA/cm2	W mpy	%IE	Surface Coverage ϴ
Blank 1N HCl	0	293	70.8	366.4	0.248	425.2	110.37	50.978	0	0
		323	145.3	185.6	1.429	513.2	116.26	53.699	0	0
		343	129	154.8	1.407	638.4	171.81	79.357	0	0
Extract	1	293	37.6	177.9	0.274	509.6	54.34	25.099	50.765	0.507
		323	101.5	184.2	1.1909	400.5	59.32	27.399	48.976	0.489
		343	164.8	202.6	2.548	364.7	108.31	50.027	36.959	0.369
Extract	5	293	68.2	163.1	1.167	537	31.37	14.489	71.577	0.715
		323	57.9	206.6	0.632	579.1	39.72	18.346	65.835	0.658
		343	75.3	133.8	0.616	592.3	87.27	40.309	49.205	0.492
Extract	10	293	84.2	201.8	1.508	593.5	29.94	13.828	72.874	0.728
		323	78.6	175.4	1.455	565.1	33.57	15.505	71.126	0.711
		343	90.3	206.7	0.944	532.5	53.08	24.517	69.105	0.691

Table 2 : The thermodynamic parameters Ea, ΔH,ΔS and ΔG For C- steel in control and in the presence of inhibitor

Comp.	conc. ppm	Ea ($KJ.mol^{-1}$)	ΔH ($KJ.mol^{-1}$)	$-\Delta S\ 10^{-3}$ ($KJ.mol^{-1}K^{-1}$)	Temp. (^{o}k)	ΔG($KJ.mol^{-1}$)
Blank (1N HCl)	0	7.341	4.738	195.894	293	62.134
					323	68.011
					343	71.929
Extract	1	8.48	5.861	196.103	293	63.319
					323	69.202
					343	73.124
Extract	5	10.4	7.781	198.584	293	65.966
					323	71.923
					343	75.895
Extract	10	15.738	13.119	203.584	293	72.769
					323	78.876
					343	82.948

Activation energy calculations

The activation energies for the corrosion process were calculated from Arrhenius type plot according to the following equation [25]:

$$W = k \exp\left(-\frac{E_a}{RT}\right) \qquad (2)$$

where Ea is the apparent activation corrosion energy, R is the universal gas constant, k is the Arrhenius pre-exponential constant and T is the absolute temperature.

Values of Ea for C-Steel in 1N HCl as control and in the presence of various concentrations of pomegranate shells extracts at three different temperatures were determined from the slope of ln(W) versus 1/T .

Typical plots are shown in Figs. (13-15) .The calculated values of Ea are listed in Table (2).

$\Delta H^0$and ΔS^0can be evaluated using the alternative formulation of the Arrhenius equation called also the transition state equation [26]:

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^0}{R}\right) \exp\left(-\frac{\Delta H_a^0}{RT}\right) \qquad (3)$$

where h is Plank's constant, N is the Avogadro number, $\Delta S^0$is the entropy of activation and ΔH^o is the enthalpy of activation. Figs (16-18) show a plot of ln(W/T) against 1/T. Straight lines are obtained with a slope of (ΔH^0a/R) and an intercept of (LnR/Nh ΔS^0 a/R) from which the values of ΔH^0 a and ΔS^0 were calculated, as listed in Table (2). The higher values of Ea and ΔH^0in the presence of extract compared to control indicate that the efficiency of the inhibitor decreases as a function of temperature . This trend is commonly known with other inhibitors. [27]. The negative value of ΔS^0 implies that the activation complex represents an association rather than a dissociation step, meaning that a decrease in disordering takes place going from reactants to the activated complex. The positive sign of the enthalpy (ΔH^0) is an endothermic nature of the steel dissolution in HCl solution. The entropy of activation (ΔS^0) in the absence of inhibitor is negative and increases with the increase concentration of the inhibitor. Values of Ea obtained in the presence of inhibitor are higher than that for the uninhibited one, indicating a strong inhibitive action for the studied compounds by increasing the energy barrier of the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on C-Steel surface [28]. The increase of Ea and ΔH^0accompanying the increase in the inhibitor concentration is explained by an increase of the energy barrier of corrosion reaction. In the case of endothermic H adsorption, with a high activation energy barrier for the transition between strongly bonded Hads and Hdiss [29].

The higher activation energy in the presence of the inhibitor further supports the proposed physiosorption mechanism.

Unchanged or lower values of Ea in inhibited systems compared to the blank to be indicative of chemisorption mechanism, while higher values of Ea suggest a physical adsorption mechanism. The standard free energy of adsorption ΔG values were calculated from the equation :

$$\Delta G=\Delta H-T\Delta S \qquad (4)$$

Where ΔH and ΔS are the variation of enthalpy and entropy of the adsorption process, the calculated values are given in Table (2). The values of ΔG obtained are presented in Table (2). Results obtained indicate that the positive value of ΔG mean the process is non-spontaneous adsorption of the pomegranate shells extract and it is strongly adsorbed on the C- steel surface , similar trend was observed with other inhibitors [30]. The increase in ΔG with the increasing concentration also indicates the strength of adsorption.

The value of ΔG indicates that the inhibitor functions by physically adsorbing on the surface of the C-Steel. The increase of ΔG with temperature reveals that the inhibition of C-Steel by the pomegranate shells extracts is an exothermic process. In the exothermic process the adsorption is unfavourable, thus increasing temperature leads to the inhibitor desorption from the C-Steel surface [31].

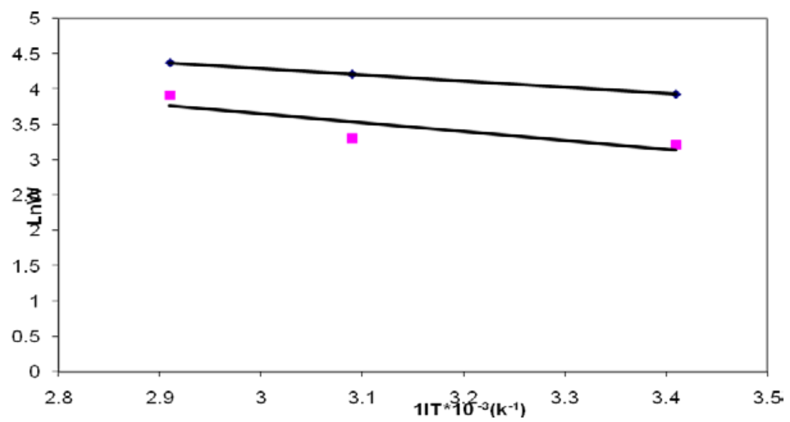


Fig. 13: Typical Arrhenius plots of ln w Vs 1/T in 1N HCl ♦ control ■ with 1ppm inhibitor

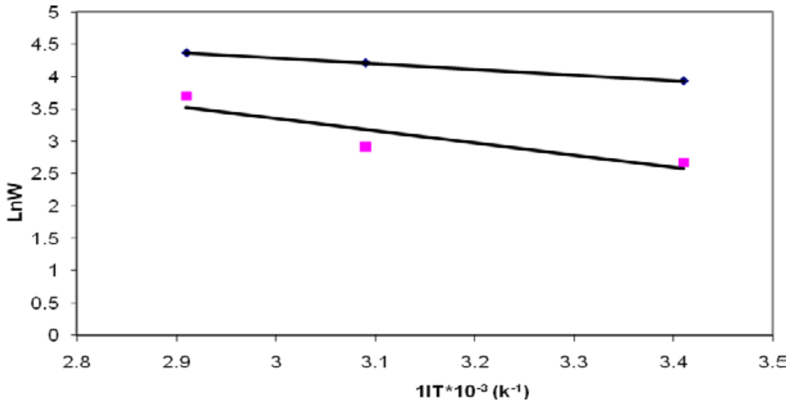


Fig. 14: Arrhenius plots of In w Vs 1/T at 1N HCL ♦ without inhibitor ■ with 5ppm inhibitor

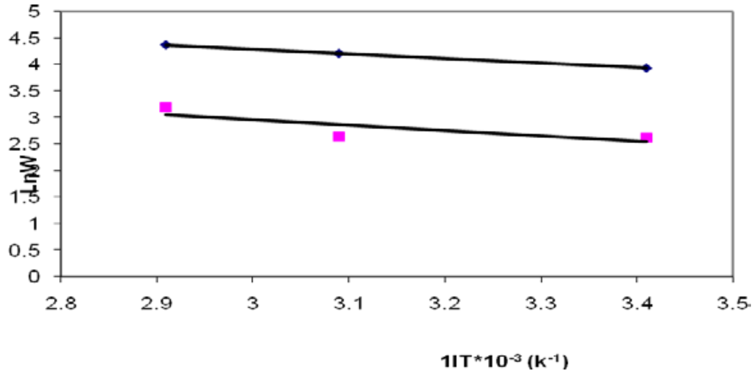


Fig. 15: Arrhenius plots of In w Vs 1/T at 1N HCL ♦ without inhibitor ■ with 10ppm inhibitor

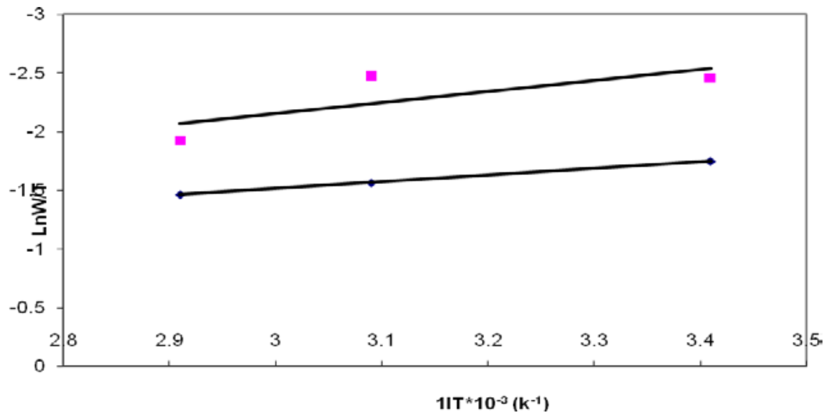


Fig.16:Typical Arrhenius plots of In w/T Vs 1/T 1N HCl ♦ without inhibitor ■ with 1ppm inhibitor

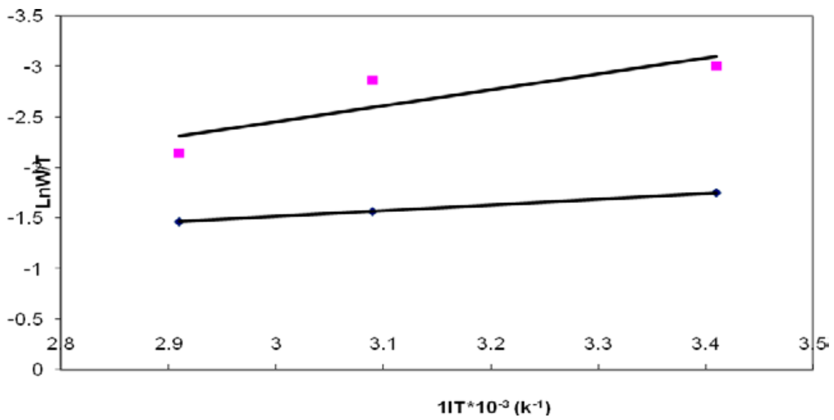


Fig.17: Arrhenius plots of In w/T Vs 1/T 1N HCL ♦ without inhibitor ■ with 5ppm inhibitor

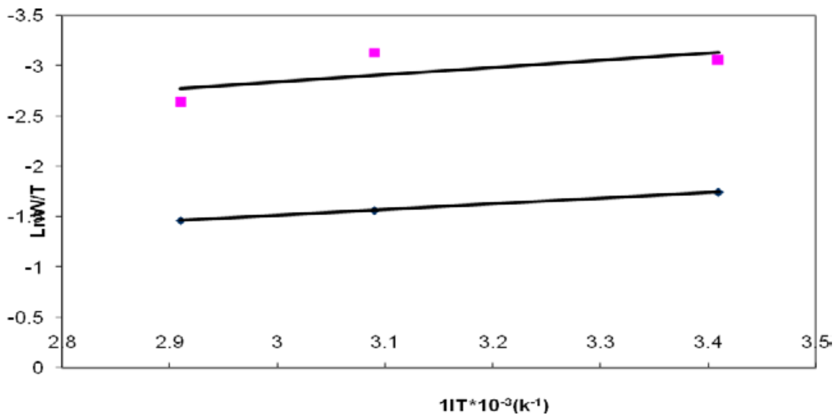


Fig. 18: Arrhenius plots of In w/T Vs 1/T 1N HCL ♦ without inhibitor ■ with 10ppm inhibitor

Surface analysis

The Electron Spectroscopy for chemical analysis (ESCA) for FT-IR surface examination was performed to obtain information on the surface coverage of the inhibitor, Fig. (19) shows ESCA of pomegranate shells extracts.

The image FT-IR spectrum of the tested sample (Coupons) after the fulfillment of the corrosion test showed the same absorption peaks at 1230 Cm^{-1} (C-N),1612 Cm^{-1} (C=N),1722 Cm^{-1} (C=O),2932 Cm^{-1} (C-H),3385 Cm^{-1} (N-H and/or OH hydrogen bonded) confirming that adsorption is highly efficient.

Scanning electron microscope (SEM) of the surface of the C-Steel specimens after conducting electrochemical test (polarization measurement) in 1 N HCl solution in the presence of pomegranate shells extracts and for the control are shown in Fig.(20). The results reveal that in the absence of pomegranate shells extracts, the C-Steel surface is damaged with pitted areas. This shape is typical pitting corrosion [32] and [33].

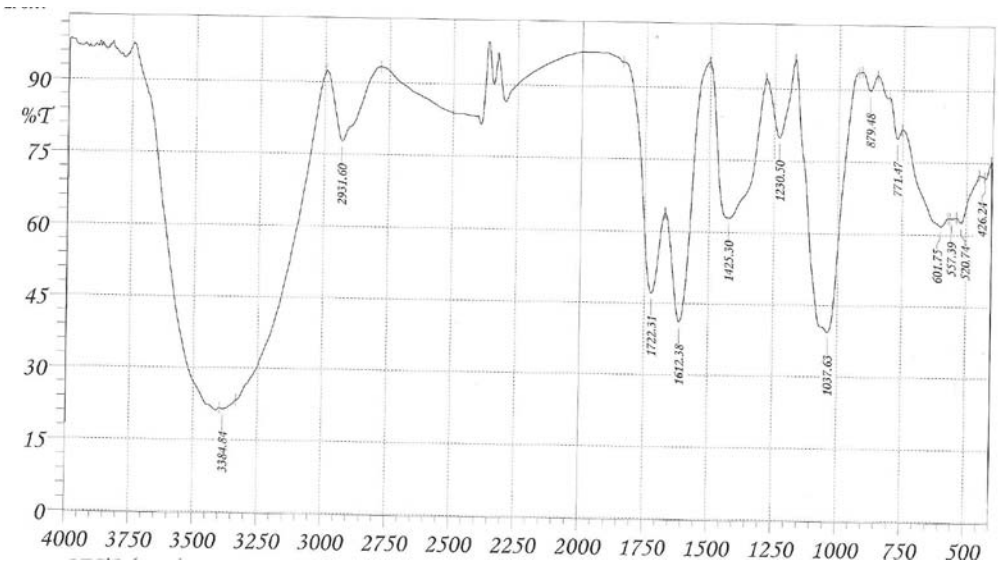
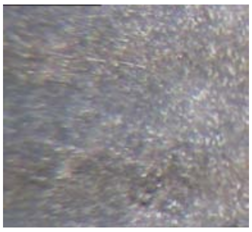


Fig. 19: FT-IR spectra of pomegranate shells extract


a


b


c


d

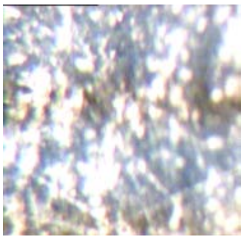

e

Fig. 20: SEM graphs of C-Steel (a) polished surface
(b) C-Steel surface immersed in 1N HCL
(c) C-Steel surface immersed in 1N HCL with 1ppm of extract
(d) C-Steel surface immersed in 1N HCL with 5ppm of extract
(e) C-Steel surface immersed in 1N HCL with 10ppm of extract

Conclusion

The pomegranate shells extracts proved to be a potential inhibitor for C-Steel in 1N HCl. The inhibition efficiency increases with inhibitor concentration and decreases with temperature. Kinetic and thermodynamic parameters indicate strong adsorption of the inhibitor alkaloid and poly hydroxyl phenols on the C-Steel surface .The inhibition mechanism is by spontaneous comprehensive adsorption (physical and chemical adsorption) of the inhibitor on C- steel surface. Electrochemical measurements confirm the mixed mode of inhibition. Thus pomegranate shells extracts proved to be an effective eco friendly and specific corrosion inhibitor.

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تأثير مستخلص قشور الرمان كمثبط تآكل طبيعي للفولاذ الكاربوني باستخدام التقنية الكهروكيميائية

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الملخص:

يتضمن البحث دراسة كفاءة مستخلص قشور الرمان كمثبطات طبيعية مانعة لتآكل الفولاذ الكاربوني في محلول 1 عياري لحامض الهيدروكلوريك عند ثلاث درجات حرارية مختلفة (293,323,343)مطلقة وعند تراكيز مختلفة. تمت الدراسة بتقنية التحليل الكهروكيميائية ودلت النتائج المستنبطة في هذه الدراسة ان كفاءة مثبط مستخلص قشور الرمان تزداد بزيادة التركيز المستخدم الا ان كفاءة التثبيط تقل بارتفاع درجة الحرارة. تشير منحنيات أستقطاب الجهد الديناميكية ان لمستخلص قشور الرمان تأثيراً تثبيطياً مزدوجاً الفعالية بسسب المركبات العضوية الفينولية والقلويدات الموجودة فيه. من ناحية اخرى اثبت دوال الدايناميك الحراري المعينة تجريبيا من منحنيات الاستقطاب حدوث حالة التوازن بين ظاهرتي الامدصاص والانحلال على سطح المعدن . يتضمن البحث ايضا القيم التجريبية التي تدعم هذه الميكانيكية للعديد من دوال الداينميك الحراري مثل طاقة التنشيط والمحتوى الحراري والعشوائية والطاقة الحرة للانحلال. تشير فحوصات المسح المجهري الالكتروني ومطيافية الاشعة تحت الحمراء لسطح الكوبونات المدروسة للمعدن ان للمثبط تأثيراً ملحوظاً في خفض شدة التآكل الملحوظة على سطح المعدن مقارنة بسطح المعدن عند غياب المثبط.وقد اشارت فحوصات مطيافية الاشعة تحت الحمراء الى امدصاص المثبط على سطح المعدن من خلال المجاميع الفعالة التي تم قياسها لاسيما مجاميع الكاربونيل والفينول والامينات.