Asian Journal of Chemistry; *Vol. 28, No. 11 (2016), 2532-2538*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.20090

Natural Products as Corrosion Inhibitor for Steel in 0.5 M Hydrochloric Acid Solution

M.A. AL-KHALDI

Department of Chemistry, College of Science, University of Dammam, P.O. Box 1982, Dammam 31441, Saudi Arabia

Corresponding author: E-mail: dr.mishaelkhaldi@yahoo.com

Received: 23 May 2016; *Accepted*: 30 July 2016; *Published online*: 10 August 2016; AJC-18034

The corrosion inhibition of steel in 0.5 M HCl by lemon leaves extracts with saffron, almonds, guava leaves and *Origanum majorana* extracts was studied using electrochemical polarization and EIS methods. The result indicate that the corrosion current density (I_{corr}) of steel increases on increasing the concentration of lemon leaves extracts while adding of each saffron, almonds, guava leaves and *Origanum majorana* extracts to solution of lemon leaves extracts in 0.5 M HCl increasing the inhibition efficiency of steel by decreasing corrosion current density and increasing charge-transfer resistance (R_{ct}) with increasing the concentration of saffron, almonds, guava leaves and *Origanum majorana* extracts in the following order: *Origanum majorana* > Guava leaves ≈ Almonds > Saffron. The effect of temperature on the corrosion behaviour of steel indicates that inhibition efficiency of the lemon leaves with saffron, almonds, guava leaves and *Origanum majorana* extracts decreases with the rise of temperature. The adsorption isotherm of inhibitors extracts on the steel has been determined and found to follow Langmuir adsorption isotherm where the negative value of free energy of adsorption indicates that the adsorption of the inhibitors components on the steel surface occurs spontaneously.

Keywords: Inhibition, Corrosion, Steel, EIS, Polarization, Lemon leaves, Saffron, Almonds, Guava leaves, *Origanum majorana*.

INTRODUCTION

Throughout the world acid solutions are commonly used for the removal of undesirable scale and rust in industrial processes. For example hydrochloric acid is widely used in the pickling of steel and ferrous alloys. The use of inhibitors is one of the most practical methods to protect against corrosion and prevent metal dissolution. Over the years, many studies have been carried out to find suitable compounds which can be used as corrosion inhibitors for the metals in different aqueous solutions. These studies revealed that the organic compounds especially containing nitrogen, sulfur and oxygen showed significant inhibition efficiency in acid solution [1-12]. Plant extracts have become an important environmentally acceptable, low-cost and readily available source of a wide range of inhibitors, they are rich sources of ingredients which have a high inhibition efficiency.

The objective of the present work was to study the effect of lemon leaves extracts with saffron, almonds, guava leaves and *Origanum majorana* extracts on the corrosion behaviour of steel. Lemon leaves can be used as a sedative and antispasmodic. Those who suffer from insomnia, nervousness and palpitation should soak five to seven leaves of lemon in a teacup of hot water and allow it to infuse for 15 min to get maximum result from the lemon leaf. Lemon leaf serves as a better alternative to valium and other synthetic relatives, which by the way, have side effects. So this study was to investigate the corrosion of mild steel in 0.5 HCl in the presence of lemon leaves extracts and the effect of adding each of saffron, almonds, guava leaves and *Origanum majorana* extracts as good inhibitors using electrochemical polarization and EIS methods.

EXPERIMENTAL

Test specimen: The working electrode is steel specimens of composed (wt %): C 0.2 %, Mn 0.6 %, P 0.04 %, Si 0.003 % and Fe 99.157 %. The metal specimens were polished with successive grades of emery papers (600 and 1200), degreased with acetone and then rinsed with running distilled water before it was immersed in the test solution.

Solution preparation method: Analytical grade 37 % HCl was used in the preparation of 0.5 M HCl solution *via* dilution with second distilled water. 3.0 g of lemon leaves was soaked in 20 mL of second distilled water at 60 °C for 24 h, blended, filtrated and then added in different amounts to 0.5 M HCl to get appropriate solutions of different lemon extract concentrations (37.5, 75, 150 and 250 ppm). Different amounts of different leaves extracts [saffron, almonds, guava (*Psidium guajava*) leaves and *Origanum majorana*] were added to a solution consisting of 75 ppm of lemon leaves and 0.5 M HCl.

Employed techniques: The electrochemical perpetuation is carried out in a conventional three-electrode glass cell. The working electrode was a steel disc has a geometric area of 1 cm^2. The reference electrode is a saturated calomel electrode (SCE) and the counter electrode is a sheet of platinum electrode of area 0.25 cm^2. The electrochemical behaviour was studied using "ACM-instrument-Gill AC" potentiostat controlled with PC at a scan rate of 200 mV min^{-1} in between –800 mV and 400 mV. Before each measurement the specimens was immersed for 1 h to attain the equilibrium potential. The response of the system (steel in absence and presence of the plant extract) was analyzed and a respective kinetic parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c, b_a) and corrosion current density (I_{corr}) were obtained. The inhibition efficiency (IE, %) was calculated using the following equation [13,14]:

$$\text{IE}\ (\%) = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100 \qquad (1)$$

where I^{o}_{corr} and I_{corr} are the corrosion current densities in absence and presence of plant extracts, respectively.

The impedance measurements (EIS) were carried out in the frequency range of (0.01-30) Hz at the open circuit potential (OCP). The spectrum, obtained by EIS, was investigated for charge-transfer resistance (R_{ct}) whose value is a measure of electron transfer across the surface and can be calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance (C_{dl}) was obtained at the frequency f_{max}, at which the imaginary component of the impedance is maximal ($-Z_{max}$), using the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad (2)$$

The inhibition efficiency percentage (IE, %) is calculated from the following equation:

$$\text{IE}\ (\%) = \frac{R_{ct\ (inh)} - R_{ct\ (acid)}}{R_{ct\ (inh)}} \times 100 \qquad (3)$$

where $R_{ct\ (inh)}$ and $R_{ct\ (acid)}$ are the charge-transfer resistance values in the presence and absence of inhibitor, respectively.

RESULTS AND DISCUSSION

Potentiodynamic polarization curves: The potentiodynamic polarization curves for steel in 0.5 M HCl with different concentrations of lemon leaves extracts at 25 °C and in 75 ppm of lemon leaves with different concentrations of saffron, almonds, guava leaves and *Origanum majorana* extracts are shown in Figs. 1-5, respectively. The respective kinetic parameters derived from potentiodynamic polarization curves such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c,b_a) and corrosion current density (I_{corr}) are given in Tables 1 and 2.

Fig. 1 (Table-1) reveals that the polarization curves are shifted towards more negative potentials and more current densities with the addition of lemon leaves extracts. This behaviour indicates that lemon leaves extract act as corrosive media for the steel. On the other hand polarization curves in Figs. 2-4 shifted towards the lower current density, the shift in current density toward lower density increases on increasing the concentration of each saffron, almonds, guava leaves and *Origanum majorana* extracts. This indicates that their compounds are adsorbed on the metal surface and hence inhibition occurs.

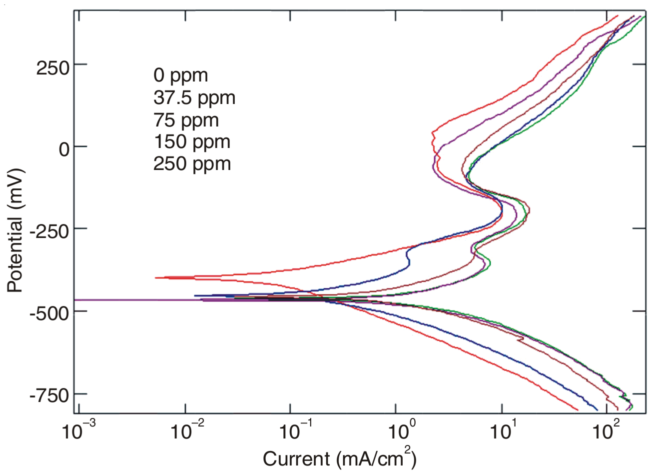

Fig. 1. Polarization curves for steel in 0.5 M HCl at different concentrations of lemon leaves extracts at 25 °C

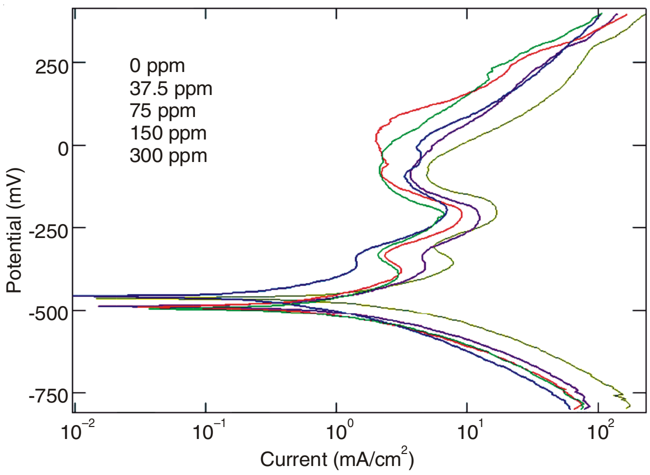

Fig. 2. Polarization curves for steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of saffron at 25 °C

TABLE-1
ELECTROCHEMICAL CORROSION PARAMETERS FOR STEEL IN 0.5 M HCl CONTAINING DIFFERENT CONCENTRATIONS OF LEMON LEAVES EXTRACTS AT 25 °C

Concentration (ppm) of lemon leaves + (0.5 M) HCl	E_{corr} (mV)	I_{corr} (mA/cm^2)	b_C (mV)	b_a (mV)
0	-399.6	0.055	111.7	68.3
37.5	-452.8	0.211	85.5	91.1
75	-465.4	0.580	56.06	56.5
150	-469.9	0.720	55.37	86.8
250	-452.0	0.809	91.91	106.2

TABLE-2
ELECTROCHEMICAL CORROSION PARAMETERS FOR STEEL IN 0.5 M HCl CONTAINING 75 ppm OF LEMON LEAVES EXTRACT AND DIFFERENT CONCENTRATION OF INHIBITOR EXTRACT AT 25 °C

Inhibitor	Conc. (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	b_c (mV)	b_a (mV)	IE (%)
Blank	–	-492.38	0.58	56.1	56.5	–
Saffron	37.5	-487.80	0.49	64.3	89.9	15.5
	75	-457.60	0.39	95.9	132.8	32.8
	150	-490.60	0.36	61.5	80.2	37.9
	250	-494.60	0.34	57.4	89.2	41.4
Almonds	37.5	-521.80	0.10	116.5	117.1	82.0
	75	-516.90	0.069	92.8	106.3	88.1
	150	-517.20	0.05	90.5	120.9	91.0
	250	-519.50	0.065	113.0	137.8	88.8
Guava leaves	37.5	-519.50	0.123	123	161.0	79.0
	75	-519.40	0.106	111.8	150.0	82.0
	150	-519.70	0.07	93	104.0	88.0
Origanum majorana	37.5	-501.40	0.071	101.5	116.8	87.7
	75	-499.08	0.069	105.7	123.5	88.1
	150	-503.60	0.061	92.5	117.9	89.4
	250	-499.00	0.046	92.4	102.6	92.0
	350	-498.00	0.040	86.5	10.8	93.0

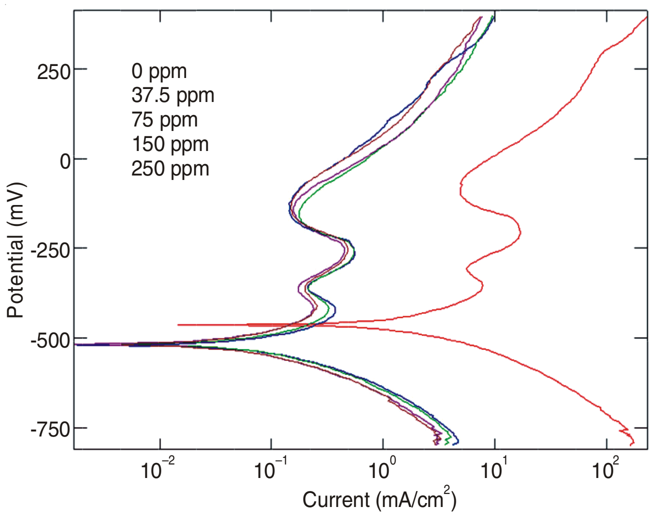

Fig. 3. Polarization curves for steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of almond extracts at 25 °C

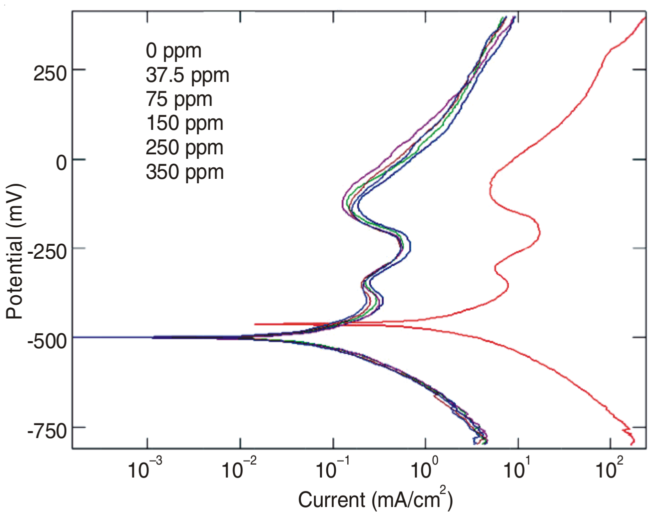

Fig. 5. Polarization curves for steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of *Origanum majorana* extracts at 25 °C

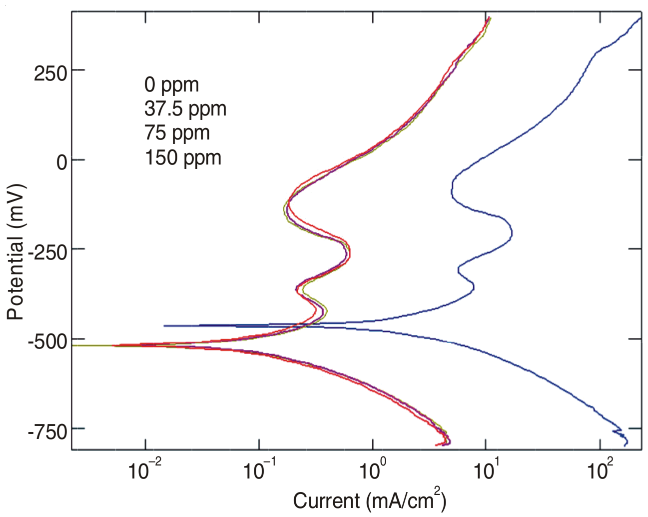

Fig. 4. Polarization curves for steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of guava leaves extracts at 25 °C

Table-2 suggests that both the anodic and cathodic Tafel constants are affected by addition of saffron, almonds, guava leaves and *Origanum majorana* extracts. This indicates that they act as a mixed inhibitor. This behaviour reflects that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of inhibitors. They hindered the acid attack on the steel electrode due to the adsorption of the organic compounds present in the extracts at the active sites of the electrode surface. It is noticed from Table-2 that the inhibition efficiency calculated from eqn. 1 increases with increasing the concentration of inhibitor extracts, but for almond at concentration more than 150 ppm the inhibition of steel corrosion decreases again this would suggest that protonated species may take part in catalyzing the hydrogen evolution reaction.

The inhibition efficiency data showed that the *Origanum majorana* molecules have greater interaction with steel compared to other additives as the following order:

Origanum majorana > Guava Leaves ≈ Almonds > Saffron

The order reflects the important role played by the molecular size and the substituent group of inhibitors molecules as well as the type of the functional adsorption atom in the inhibition processes [15-18].

Electrochemical impedance measurements (EIS): Impedance spectra for steel in 0.5 M HCl containing different concentrations of lemon leaves extracts and 75 ppm of lemon leaves with different concentration of each saffron, almonds, guava leaves and *Origanum majorana* extracts are given in Figs. 6-10, respectively. The impedance diagram (Nyquist) contains a depressed semicircle with the center under the real axis, such behaviour is characteristic for solid electrodes and often referred to frequency dispersion have been attributed to roughness and inhomogeneities of solid surface. The plots indicate that the process occurs under activation control.

Tables 3 and 4 collects various parameters such as charge-transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) using the eqn. 2. And the inhibition efficiency percentage (%IE) got from the charge-transfer resistance is calculated from eqn. 3.

It is clear from Table-3 that the charge-transfer resistance R_{ct} whose inversely proportional to corrosion rate I_{corr}, decreases and the pseudo capacity C_{dl} increases on increasing lemon leaves extracts concentration, which indicate that the lemon leaves compounds may take part in catalyzing the hydrogen evolution reaction. On the other hand (Table-4) R_{ct} for adding saffron, almonds, guava leaves and *Origanum majorana* extracts

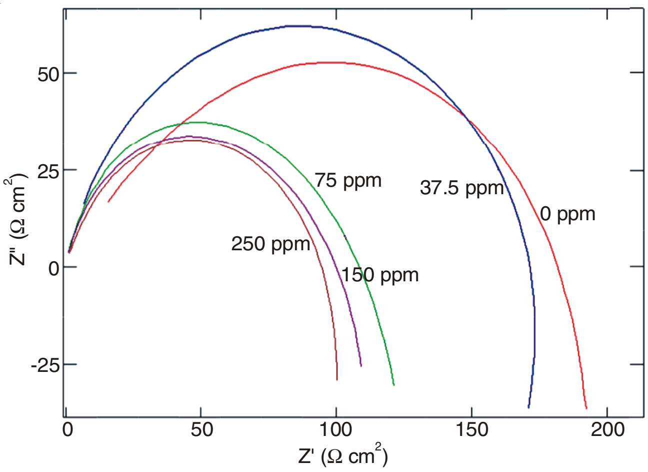

Fig. 6. EIS curves of steel in 0.5 M HCl containing different concentrations of lemon leaves extracts at 25 °C

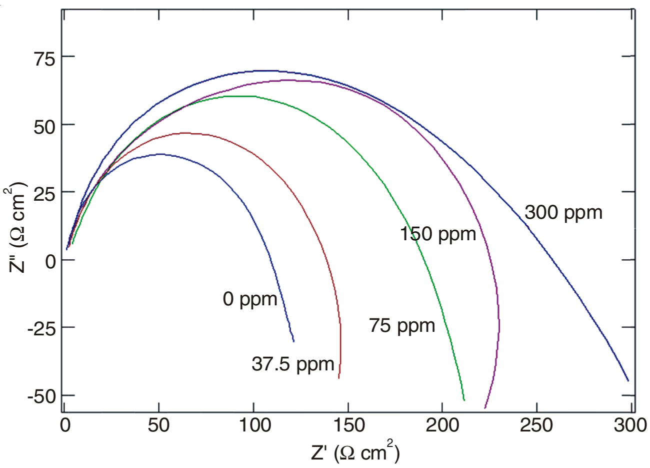

Fig. 7. EIS curves of steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of saffron extract at 25 °C

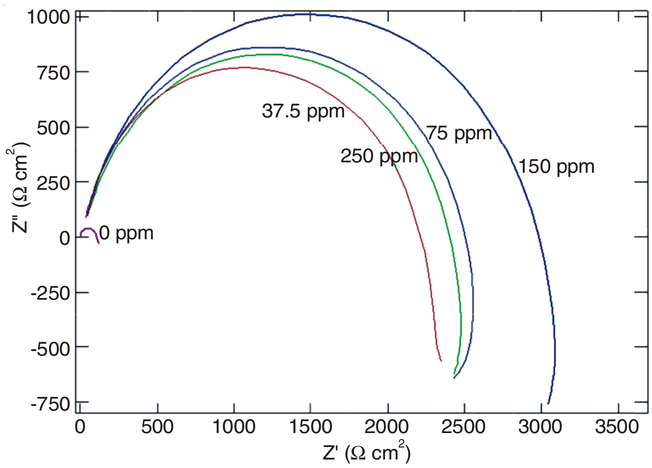

Fig. 8. EIS curves of steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of almonds extracts at 25 °C

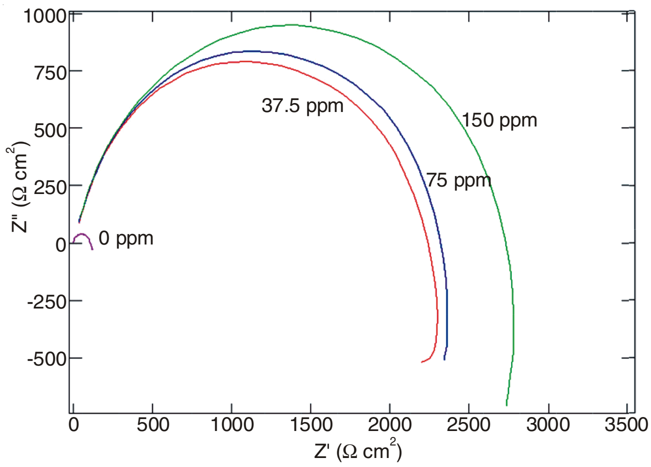

Fig. 9. EIS curves of steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of guava leaves extracts at 25 °C

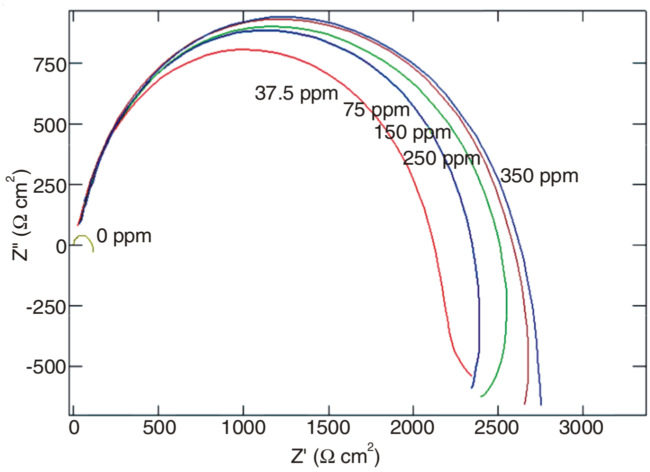

Fig. 10. EIS curves of steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of *Origanum majorana* leaves extracts at 25 °C

TABLE-3
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR STEEL IN 0.5 M HCl CONTAINING DIFFERENT CONCENTRATIONS OF LEMON LEAVES EXTRACTS AT 25 °C

	Concentration (ppm) of lemon leaves extract + 0.5 M HCl				
	0	37.5	75	150	250
R_{ct} (Ω cm^2)	2.3×10^2	1.7×10^2	1.1×10^2	0.81×10^2	0.80×10^2
C_{dl} (μF/cm^2)	1.8×10^{-3}	0.8×10^{-3}	2.2×10^{-3}	2.3×10^{-3}	2.69×10^{-3}

to lemon leaves solution increases and C_{dl} decreases because they inhibit the corrosion rate of steel by an adsorption mechanism. These results suggested that the formed inhibitive film was strengthened as the concentration was increased [19] these results confirm the results obtained above from the polarization measurements.

TABLE-4
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR STEEL IN 0.5 M HCl CONTAINING 75 ppm OF LEMON LEAVES EXTRACT AND DIFFERENT CONCENTRATION OF INHIBITOR EXTRACT AT 25 °C

Inhibitor	Conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	θ	IE (%)
Blank		1.2×10^2	0.72		
Saffron	37.5	1.46×10^2	3.05×10^{-3}	0.178	17.8
	75	1.83×10^2	2.59×10^{-3}	0.340	34.0
	150	2.20×10^2	2.10×10^{-3}	0.454	45.4
	250	2.55×10^2	2.40×10^{-3}	0.530	53.0
Almonds	37.5	2.22×10^3	1.42×10^{-4}	0.945	94.5
	75	2.50×10^3	1.38×10^{-4}	0.952	95.2
	150	2.90×10^3	1.19×10^{-4}	0.958	95.8
	250	2.40×10^3	1.28×10^{-4}	0.950	95.0
Guava leaves	37.5	2.06×10^3	1.19×10^{-4}	0.942	94.2
	70	2.21×10^3	1.20×10^{-4}	0.945	94.5
	150	2.47×10^3	1.04×10^{-4}	0.951	95.1
Origanum majorana	37.5	2.14×10^3	1.28×10^{-4}	0.943	94.3
	75	2.35×10^3	1.16×10^{-4}	0.948	94.8
	150	2.52×10^3	1.13×10^{-4}	0.952	95.2
	250	2.57×10^3	1.10×10^{-3}	0.953	95.3
	350	2.60×10^3	1.11×10^{-3}	0.954	95.4

Adsorption isotherm: The adsorption mode of inhibitors on the steel surface in the given medium must be defined by the relationship between concentration of inhibitor extracts (C) and fraction of steel surface coverage (θ) by the adsorbed compound. The degree of surface coverage, (θ), at different concentration of inhibitor extract (saffron, almonds, guava leaves and *Origanum majorana*) C_{inh} in 0.5 M HCl containing 75 ppm of lemon leaves was evaluated from electrochemical impendence measurement (Table-4) using the following equation:

$$\theta = \frac{R_{ct\,(inh)} - R_{ct\,(acid)}}{R_{ct\,(inh)}} \tag{4}$$

The data was tested graphically, the best fit was obtained for the relation between C_{inh}/θ and C_{inh} which represented in Fig. 11. The data indicate that the adsorption process follows Langmuir adsorption isotherm. The plot is linear with high correlation coefficient (0.9). Langmuir adsorption isotherm could be represented using the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{5}$$

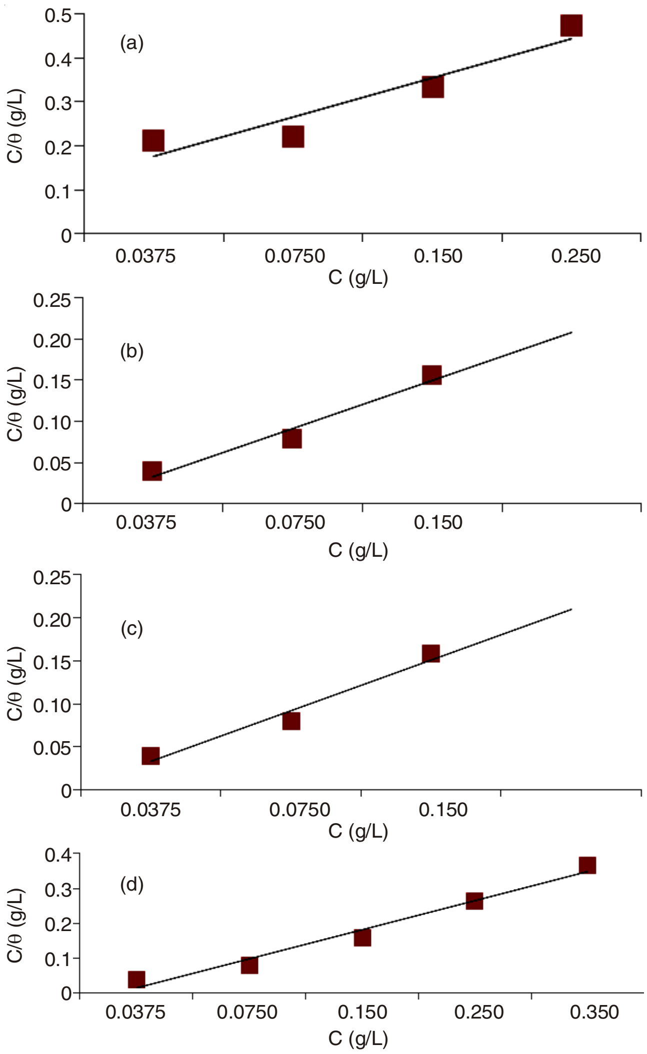

Fig. 11. Langmuir adsorption plot for steel in 0.5 M HCl containing 75 ppm of lemon leaves extract and different concentration of (a) Saffron extract; (b) Almonds extracts; (c) Guava leaves extracts and (d) *Origanum majorana* extracts at 25 °C

where K_{ads} is the equilibrium constant of the adsorption process [20]. Free energy of adsorption ΔG_{ads}, can be calculated by eqn. 6. The numeral of 55.5 is the molar concentration of the solution in water:

$$\ln K_{ads} = \ln \frac{1}{55.5} - \frac{\Delta G_{ads}}{RT} \tag{6}$$

The values for adsorption of saffron, almonds, guava leaves and *Origanum majorana* extracts were found to be –16.03, –19.04, –19.02, –16.51 kJ mol^{-1}, respectively.

The negative value suggests that the adsorption of inhibitors components on the steel surface is a spontaneous process. Literature survey [21,22] reveals that the values around –20 kJ mol^{-1} or, lower are consistent with the electrostatic inter-

TABLE-5
CORROSION PARAMETERS OBTAINED FROM POLARIZATION CURVE AND EIS OF STEEL IN LEMON LEAVES (37.5 ppm) AND LEMON LEAVES WITH SAFFRON (20 ppm) AND ALMONDS (20 ppm) IN 0.5 M HCl AT DIFFERENT TEMPERATURES

Temp. (K)	Solution	E_{corr} (mV)	I_{corr} (mA/cm^2)	R_{ct} (Ω cm^2)	IE (%)
293	Lemon leaves	-526.2	0.081	2.01×10^3	–
	Saffron + lemon leaves	-521.7	0.051	2.17×10^3	37.0
	Almonds + lemon leaves	-521.53	0.037	2.25×10^3	54.3
308	Lemon leaves	-526.3	0.11	1.07×10^3	–
	Saffron + lemon leaves	-526.4	0.07	1.70×10^3	36.0
	Almonds + lemon leaves	-519.4	0.049	1.80×10^3	54.0
318	Lemon leaves	-455.2	0.18	0.17×10^3	–
	Saffron + lemon leaves	-505.5	0.12	0.62×10^3	33.0
	Almonds + lemon leaves	-507.7	0.09	0.78×10^3	50.0

action between the charged molecules and the charged metal (physical adsorption) [19] while those negative than 40 kJ mol^{-1} involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [20]. In this study, the values of ΔG_{ads} are between –16.03 and –19.04 which suggests that the adsorption mechanism of inhibitors on steel is physical adsorption.

Effect of temperature: The effect of temperature on inhibition efficiencies of saffron and almonds extracts was studied in the temperature range 20-45 °C in 0.5 M HCl with lemon leaves using polarization measurements (Table-5). Inspection of Table-5 reveals that the corrosion rates of steel in lemon leaves and lemon leaves with saffron and almonds extracts increased as the temperature was increased but is more pronounced for lemon leaves extract solution, the values of inhibition efficiency decreases slightly with increase in the temperature. The apparent activation energies E_a of the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation:

$$k = A.\exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where E_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant, and k is the rate constant, which is directly proportion to the corrosion current (I_{corr}). Values of E_a for steel in lemon leaves and lemon leaves with saffron and almonds extracts were determined from the slope of ln I_{corr} *versus* 1/T plots (Fig. 12). The values of activation energy are 23.7 kJ mol^{-1}, 25.4 kJ mol^{-1} and 26.2 kJ mol^{-1}, respectively. The obtained results suggest that saffron and almonds extracts inhibit the corrosion reaction by increasing its activation energy. The higher activation energy value in the presence of almonds supports the results obtained from polarization measurements and EIS.

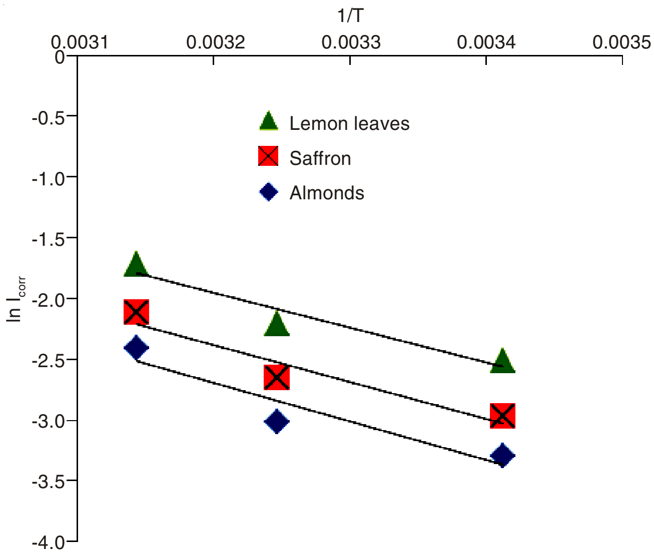

Fig. 12. Arrhenius slops calculated from corrosion current density for steel in 0.5 M HCl for lemon leaves extract and lemon leaves extract with saffron and almonds

Conclusions

• The aqueous extract of lemon leaves acts as corrosive media for the steel.

• Saffron, almonds, guava leaves and *Origanum majorana* extracts with lemon leaves extract as a good inhibitors for the corrosion of steel in 0.5 M HCl.

• The inhibition efficiency of the inhibitor increases with the concentration increases.

• The addition of saffron, almond, guava leaves and *Origanum majorana* supported the corrosion inhibition action in acidic media with the flowing order:

Origanum majorana > Guava leaves ≈ Almonds > Saffron

• Aqueous extract saffron, almonds, guava leaves and *Origanum majorana* extracts act as a mixed inhibitor.

• The adsorption process of inhibitors extracts follow Langmuir adsorption isotherm.

ACKNOWLEDGEMENTS

The author thanks Deanship of Scientific Research in University of Dammam, Saudi Arabia, for supporting this work and funding this project [Grant No. 2014084].

REFERENCES

1. M.M. El-Naggar, *Corros. Sci.*, **49**, 2226 (2007).
2. K.O. Orubite and N.C. Oforka, *Mater. Lett.*, **58**, 1768 (2004).
3. G. Gunasekaran and L.R. Chauhan, *Electrochim. Acta*, **49**, 4387 (2004).
4. A.Y. El-Etre, M. Abdallah and Z.E. El-Tantawy, *Corros. Sci.*, **47**, 385 (2005).
5. Y. Li, P. Zhao, Q. Liang and B. Hou, *Appl. Surf. Sci.*, **252**, 1245 (2005).
6. P.B. Raja and M.G. Sethuraman, *Mater. Lett.*, **62**, 113 (2008).
7. A.M. Abdel-Gaber, B.A. Abd-El-Nabey and M. Saadawy, *Corros. Sci.*, **51**, 1038 (2009).
8. M.A. Quraishi, A. Singh, V.K. Singh, D.K. Yadav and A.K. Singh, *Mater. Chem. Phys.*, **122**, 114 (2010).
9. O.K. Abiola and A.O. James, *Corros. Sci.*, **52**, 661 (2010).
10. M.A. Ameer, *Mater. Chem. Phys.*, **122**, 321 (2010).

11. V.V. Torres, R.S. Amado, C.F. de Sá, T.L. Fernandez, C.A.S. Riehl, A.G. Torres and E. D'Elia, *Corros. Sci.*, **53**, 2385 (2011).
12. S. Deng and X. Li, *Corros. Sci.*, **55**, 407 (2012).
13. E. Bayol, K. Kayakýrýlmaz and M. Erbil, *Mater. Chem. Phys.*, **104**, 74 (2007).
14. L. Tang, G. Mu and G. Liu, *Corros. Sci.*, **45**, 2251 (2003).
15. M. Abdallah, I. Zaafarany, K.S. Khairou and Y. Emad, *Chem. Technol. Fuels Oils*, **48**, 234 (2012).
16. S. Noyel Victoria and R. Rohith Prasad, *Int. J. Electrochem. Sci.*, **10**, 2220 (2015).
17. T.Y. Soror, *Eur. Chem. Bull.*, **2**, 191 (2013).
18. R. Oukhrib, S. El Issami, A. Chaouay, K. El Mouaden, A. Jmiai, B.E.L. Ibrahimi, L. Bazzi, L. Bammou and M. Hilali, *Chem. Sci. Rev. Lett.*, **4**, 241 (2015).
19. S.T. Zhang, Z. Tao, W. Li and B. Hou, *Appl. Surf. Sci.*, **255**, 6757 (2009).
20. S.M.A. Hosseini and A. Azimi, *Corros. Sci.*, **51**, 728 (2009).
21. J.C. da Rocha, J.A. da Cunha Ponciano Gomes and E. D'Elia, *Corros. Sci.*, **52,** 2341 (2010).
22. M.H. Hussin and M.J. Kassim, *Mater. Chem. Phys.*, **125**, 461 (2011).