Int. J. Electrochem. Sci., 10 **(2015)** 4366 - 4380

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Corrosion Behavior of Mild Steel in HCl and H_2SO_4 Solutions in Presence of Loquat Leaf Extract

Khadija M. Hijazi[1], *A. M. Abdel-Gaber*[1,2,*], *G. O. Younes*[1]

[1] Department of Chemistry, Faculty of Science, Beirut Arab University, Lebanon
[2] Department of Chemistry, Faculty of Science, Alexandria University, Ibrahimia, P.O. Box 426, Alexandria 21321, EGYPT
[*]E-mail: ashrafmoustafa@yahoo.com; a.abdelgaber@bau.edu.lb

Received: 19 January 2015 / *Accepted:* 6 March 2015 / *Published:* 23 March 2015

The electrochemical corrosion behavior of mild steel in 0.5 M HCl and 0.5M H_2SO_4 solutions in presence of loquat, *Eriobotrya japonica* [EB], leaf extract was studied using potentiodynamic polarization, electrochemical impedance spectroscopy and Fourier infrared spectroscopy (FTIR) measurements. Tafel polarization studies revealed that EB acts as mixed type in hydrochloric and anodic type inhibitor in sulphuric acid solution. The impedance response consisted of characteristic depressed semicircles clarifying that the corrosion process occurs under charge transfer control. The inhibition efficiency of the leaf extract increased with increasing the concentration and decreased with temperature. The results showed that EB is more efficient in 0.5 M HCl than in 0.5M H_2SO_4 solutions. Theoretical fitting of Temkin isotherm was tested to clarify the nature of adsorption on mild steel surface. Thermodynamic parameters indicated that the inhibition of corrosion of mild steel by EB leaf extract occurred by physical adsorption mechanism.

Keywords: steel, electrochemistry, corrosion, inhibition, *Eriobotrya japonica* leaf extract

1. INTRODUCTION

The study of corrosion inhibition of mild steel using green inhibitor in acidic media, containing HCl or H_2SO_4 in particular, is one of the important topics of current researches. Due to the aggressiveness of these acids which results in rapid corrosion of metallic parts and hence a substantial economic loss; many organic compounds have been studied and employed as corrosion inhibitors [1, 2]. Inhibitors are used in various industries including chemical cleaning, acid pickling and acid descaling as well as oil well acidification [3]. Although these organic inhibitors are effective but they are generally toxic and can cause many severe environmental hazards. Therefore, it is interesting to note that in the field of corrosion inhibition we are going back to the past as a result of the fact that increasing awareness of health and ecological risks is drawing attention to finding more suitable non-toxic inhibitors, which are found mostly among the class of natural products. Hence the use of natural products as eco-friendly and harmless corrosion inhibitors is gaining an increasing popularity [4]. Many research groups have reported the successful use of naturally plant-derived substances to restrain the metal corrosion [5, 6]. The plant extracts of Oxandra asbeckii [7], ginkgo [8] and Neolamarckia cadamba [9] have been reported as good inhibitors for acidic corrosion.

The aim of the present work is to study the electrochemical behavior of steel in acidic medium containing EB leaf extract and studying its inhibiting properties and adsorption mechanism.

2. EXPERIMENTAL

2.1. Solution preparation.

The test solutions were prepared from distilled water and analytical grade reagent HCl and H_2SO_4 from BDH chemical company. Stock solution of plant extracts was obtained by drying the plant leaf for 2 h in an oven at 80^oC and grinding to powdery form. A 10 g sample of the powder was refluxed in 100 mL distilled water for 1 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determined by evaporating 10 mL of the filtrate and weighing the residue. Prior each experiment, 4M HCl or H_2SO_4 is added to an appropriate volume of the stock solution of plant leaf extract and double distilled water to obtain a solution of 0.5M HCl or 0.5M H_2SO_4 solutions and the required concentration of the extract.

2.2. Electrochemical studies.

Electrochemical impedance and polarization measurements were achieved using frequency response analyzer (FRA)/potentiostat supplied from ACM instruments (UK). The frequency range for electrochemical impedance spectroscopy (EIS) measurements was 0.1 to $3x10^4$ Hz with applied potential signal amplitude of ±10mV around the rest potential. The data were obtained in an electrochemical cell of three-electrode mode; platinum wire and saturated calomel electrodes (SCE) were used as counter and reference electrodes. The material used for constructing the working electrode was mild steel of the following chemical composition (wt. %) (C:0.198 ,Mn:0.57,Si:0.085 ,S:0.038 ,P:0.02 ,and Fe:98.8). The steel plate of rectangular shape was encapsulated in Teflon in such a way that only one surface was left uncovered. The exposed area ($0.36cm^2$) was mechanically abraded with a series of emery papers of variable grades, starting with a coarse one and proceeding in steps to the finest (800) grade. Before polarization and EIS measurements, the working electrode was left for 30 min to attain the open circuit potential in the used solution. Polarization curve measurements were obtained by polarizing the working electrode from -250 mV cathodically to +250 mV anodically with respect to open circuit potential at a scan rate of 30mV/min. All the measurements were done at 30 ± 0.1 ^0C using WiseCircu water bath (Germany) in solutions open to the atmosphere under unstirred conditions. To obtain the activation parameters the measurements were carried out at 30-60^oC. To test the reliability and reproducibility of the measurements, duplicate experiments were performed under the same conditions in each case and found to be within 2% error.

2.3. FTIR analysis

The Infrared spectra of the solid sample were recorded by averaging 32 scans at a resolution of 4cm^{-1} using a Perkin-Elmer (2000 FTIR) spectrometer in the spectral region between 4000 and 500 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves

Figures 1 and 2 show the potentiodynamic polarization curves for steel in 0.5 M HCl and 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of Eriobotrya japonica (EB) leaf extract. Figure 1 explains that EB leaf extract retard both metal dissolution of steel in 0.5 M HCl solution and hydrogen evolution processes indicating that it acts as mixed type inhibitor. On the other hand, figure 2 clarifies that EB leaf extracts suppress the anodic part of polarization curve of steel in 0.5 M H_2SO_4 showing that it acts as anodic type inhibitor.

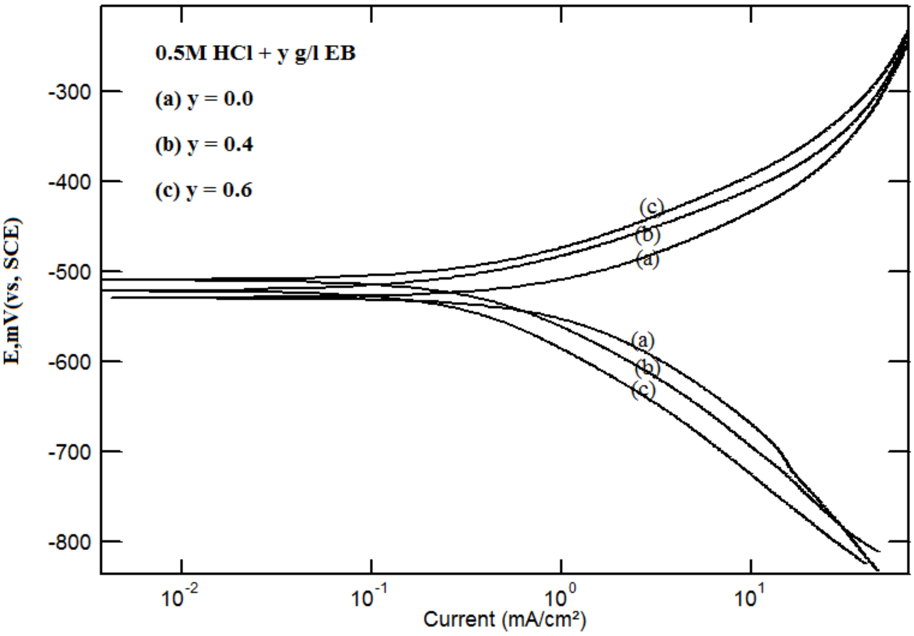

Figure 1. Potentiodynamic polarization curves for steel in 0.5 M HCl solutions in the absence and the presence of different concentrations of Eriobotrya japonica (EB) leaf extract at 30°C.

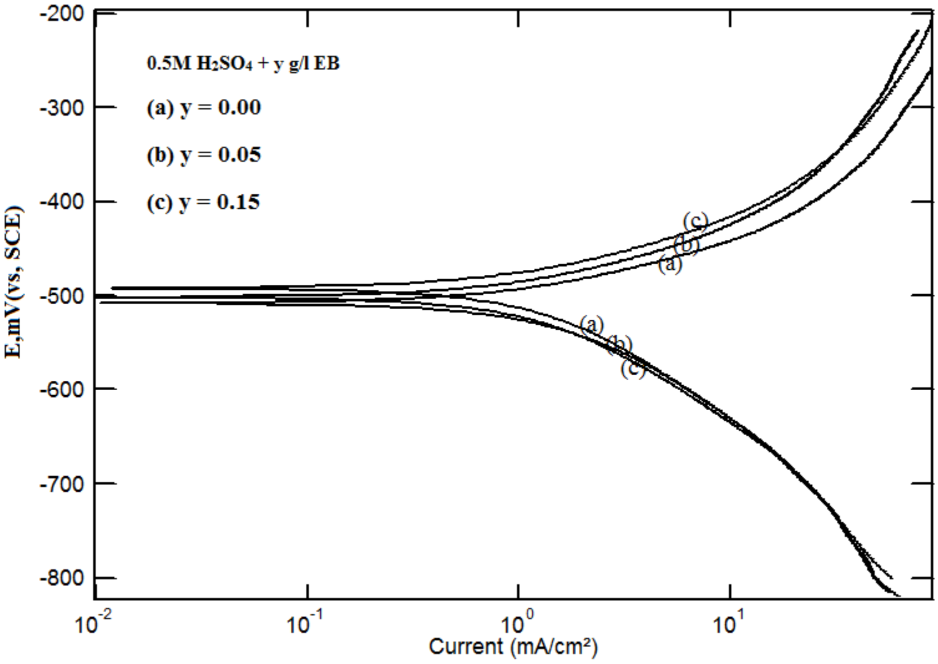

Figure 2. Potentiodynamic polarization curves for steel in 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of Eriobotrya japonica (EB) leaf extract at 30°C.

Table 1. The electrochemical corrosion parameters for steel in in 0.5 M HCl and 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of *Eriobotrya japonica* (EB) leaf extracts at 30^{o}C.

Acid Solution	Conc. (ppm)	E_{corr} (mV vs. SCE)	β_a	β_c	i_{corr} (mA cm^{-2})	η
			mV/decade			
0.5M HCl	0.00	-520	106	131	1.519	-
	200	-525	81	121	0.744	51
	300	-510	81	120	0.660	57
	400	-513	77	112	0.56	63
	600	-524	69	117	0.448	71
	700	-519	75	114	0.340	76
0.5M H_2SO_4	0.00	-509	82	154	1.55	-
	50	-503	79	132	1.30	16.0
	100	-493	82	137	1.11	28.4
	150	-492	76	138	1.01	35.0
	200	-493	66	145	0.95	38.7
	250	-489	69	132	0.87	44.0
	300	-491	77	143	0.99	34.8

The electrochemical corrosion parameters; corrosion current density, icorr; corrosion potential, E_{corr}; and cathodic and anodic Tafel slopes (β_c and β_a) along with the percentage of inhibition efficiency, η, for steel in 0.5 M HCl and 0.5 M H_2SO_4 solutions in the absence and the presence of different concentrations of *Erioboteya japonica* (EB) leaf extracts at 30^{o}C are listed in Table 1. The η was calculated from polarization measurements using the relation

$\eta = [(i_0-i)/i_0] \times 100$

where i_o and i, are the corrosion current density in the absence and the presence of EB leaf extract.

Inspection of Table 1 reveals that that i_{corr} decreases and η increases with increasing the concentration of the EB leaf extract indicating that the EB leaf extract inhibit the corrosion of steel in 0.5M HCl, and 0.5M H_2SO_4. Moreover, addition of EB leaf extracts slightly affect E_{corr} of steel in 0.5M HCl indicating that it could be classified as pickling type inhibitor [10]. The slight variations in anodic and cathodic Tafel slopes (βa) and (βc), in the presence of the EB leaf extracts, indicates that the inhibiting action is taking place by the simple blocking of the available cathodic and/or anodic sites on the metal surface [11].

Figure 3 shows the variations of degree of surface coverage ($\theta = \eta/100$) obtained from potentiodynamic polarization measurements with the leaf extract concentration. In HCl solution, the variations of degree of surface coverage is characterized by an initial rising part followed by an approximately constant saturated part at high concentrations, indicating the formation of mono-layer films on the mild steel surface. On the other hand, in H_2SO_4 solution, the appearance of critical concentration after which the inhibitive effect of extract decreased is also observed. The curves also indicate that EB is more effective in in 0.5M HCl than 0.5M H_2SO_4 solutions.

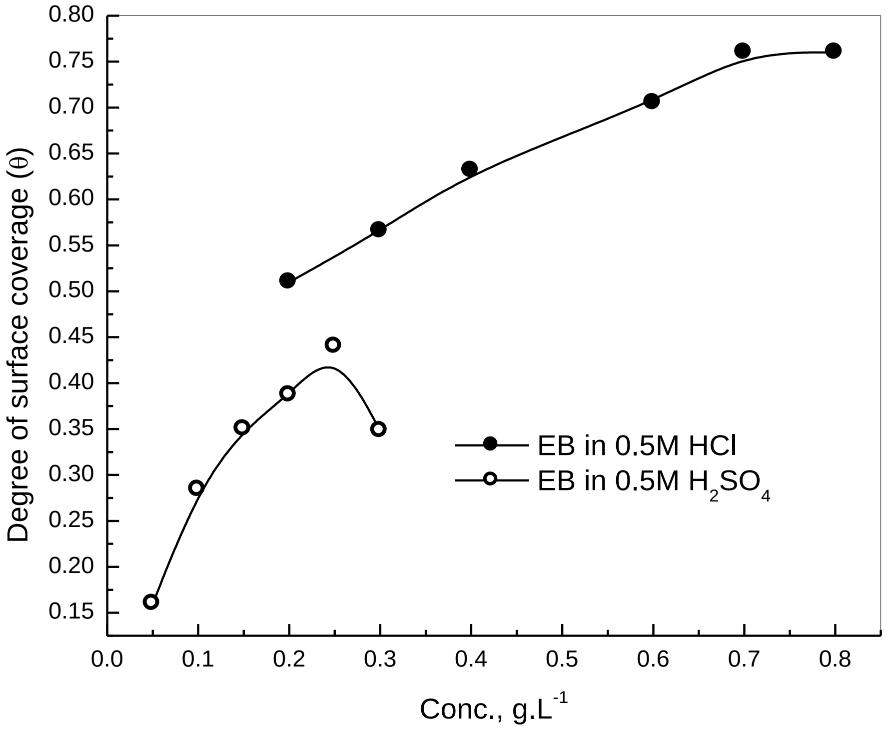

Figure 3. The variations of degree of surface coverage, obtained from polarization measurements, with the leaf extract concentration.

3.2. Electrochemical impedance spectroscopy measurements

Figures 4 and 5 show Nyquist impedance plots of steel in 0.5M HCl and 0.5M H_2SO_4 in the absence and the presence of different concentrations of EB leaf extracts. The impedance response consisted of characteristic depressed semicircles clarifying that the corrosion process occurs under charge transfer control. These semicircles are of capacitive type whose size increases with increasing EB leaf extract concentrations.The similarity of the observed semicircular in the blank and in presence of different concentrations of EB leaf extract indicated that the corrosion mechanism remained the same irrespective of the presence or absence of the inhibitor [6, 12].

The impedance spectra for different Nyquist impedance plots were analyzed in terms of the equivalent circuit model represented in Figure 6 which includes the solution resistance R_s and constant Phase Element (CPE) which is placed in parallel to charge transfer resistance element, R_{ct} [13-15]. The (R_{ct}) value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate.

To compensate for non-homogeneity in the system, the capacitances were implemented as a constant Phase Element (CPE) that is defined by two values, the non ideal double layer capacitance (Q_{dl}) and a constant n. For a non-homogeneous system, n values ranges from 0.9 to 1[16].The impedance, Z, of CPE is presented by [17]:

$$Z_{CPE} = Q_{dl}^{-1}(i\omega)^{-n}$$

Where $i = (-1)^{1/2}$, ω is the frequency in rad s^{-1}, $\omega = 2\pi f$, and f is the frequency in Hz. If n equals 1, then, Z_{CPE} is identical to that of a capacitor, $Z_C = (i\omega C)^{-1}$, where C is the capacitance. In fact, a capacitor is actually a constant phase element with a constant phase angle of 90.

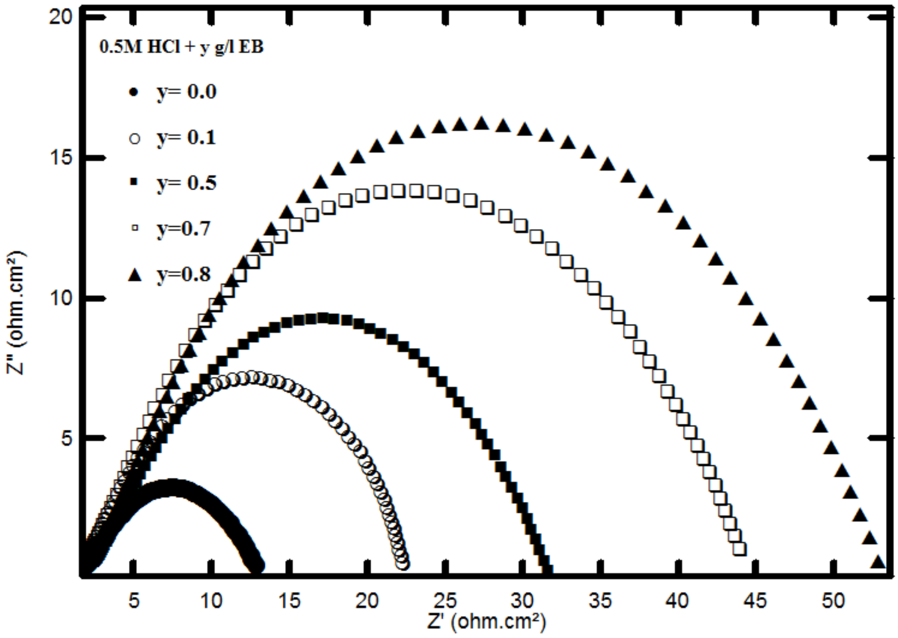

Figure 4. Nyquist Impedance plots for mild steel in 0.5M HCl in the absence and the presence of different concentrations of EB leaf extracts at 30°C.

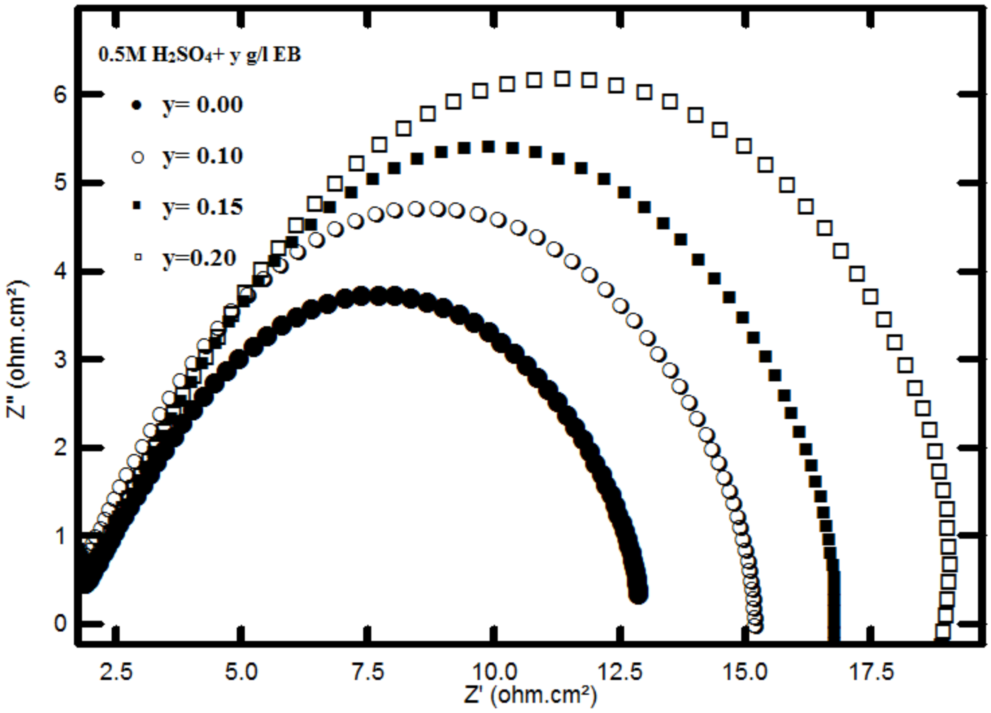

Figure 5. Nyquist Impedance plots for mild steel in 0.5M H_2SO_4 in the absence and the presence of different concentrations of EB leaf extracts at 30°C.

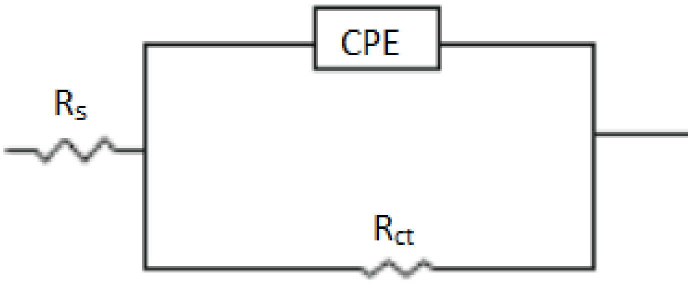

Figure 6. schematic for the equivalent circuit model

The values of electrochemical impedance parameters, charge transfer resistance (R_{ct}), the non-ideal double layer capacitance (Q_{dl}) together with n values obtained from fitting of the experimental data to the used equivalent circuit model are presented in Table 2. The percentage inhibition efficiency (η) can be calculated from impedance measurements according to the equation:

$$\eta = [(R_{ct} - R_{ct0})]/R_{ct} \times 100$$

where R_{ct0} and R_{ct} are the values of the charge transfer resistance (Ω cm^2) in the absence and the presence of leaf extract, respectively.

Table 2. Impedance parameters for mild steel in 0.5M HCl and 0.5M H_2SO_4 containing different concentrations of EB leaf extracts at 30°C.

Acid Solution	Conc. (ppm)	R_{ct} (Ω cm^2)	Q_{dl} (μF)	n	η
0.5M HCl	0	10.67	1212.5	0.75	0
	100	21.88	915.8	0.79	50
	200	22.45	925.5	0.82	52
	300	24.54	910.1	0.78	57
	400	27.02	908.6	0.79	61
	500	29.18	900.3	0.78	63
	600	37.57	782.7	0.77	72
	700	42.61	628.0	0.78	75
	800	44.85	715.9	0.87	76
0.5M H_2SO_4	0	11.52	142	0.77	0
	50	13.60	154	0.74	15.3
	100	15.61	139	0.71	26.2
	150	16.98	741	0.75	32.0
	200	18.47	703	0.76	38.0
	250	19.83	780	0.78	42.0

The data indicate that, for 0.5M HCl, increasing EB leaf extract concentration increases the R_{ct} and η; and decreases Q_{dl}. The change in the R_{ct} and Q_{dl} values is due to the gradual replacement of water molecules by the anions of the acid and by the adsorption of the organic molecules on the metal surface, decreasing the extent of the metal dissolution [18]. On the other hand, for 0.5M H_2SO_4, the increase in the Q_{dl} values indicate that the leaf extract inhibit the corrosion of steel in sulphuric acid solution by the adsorption/desorption mechanism. The adsorption/desorption equilibrium is most probably shifted towards desorption. But the concentration of the inhibitor is high enough to sustain an inhibiting adsorption layer [19]. It may be assumed that the density of the layer of adsorbed particles within outer Helmholtz layer (OHL) decreases while the diffuse part of double electrical layer increases. It is clear that, the inhibition efficiencies calculated from EIS are in good agreement with those obtained from potentiodynamic polarization curves.

3.3. Spectrophotometric analysis

Figure 7 shows the FTIR spectrums of EB leaf extracts. The IR spectrum showed absorption bands for secondary NH (3305.6 cm^{-1}), C-H stretching vibration (2918.3cm^{-1}), C=N (1605). The strong band around 1039.7 cm^{-1} is assigned to C-O single bond.

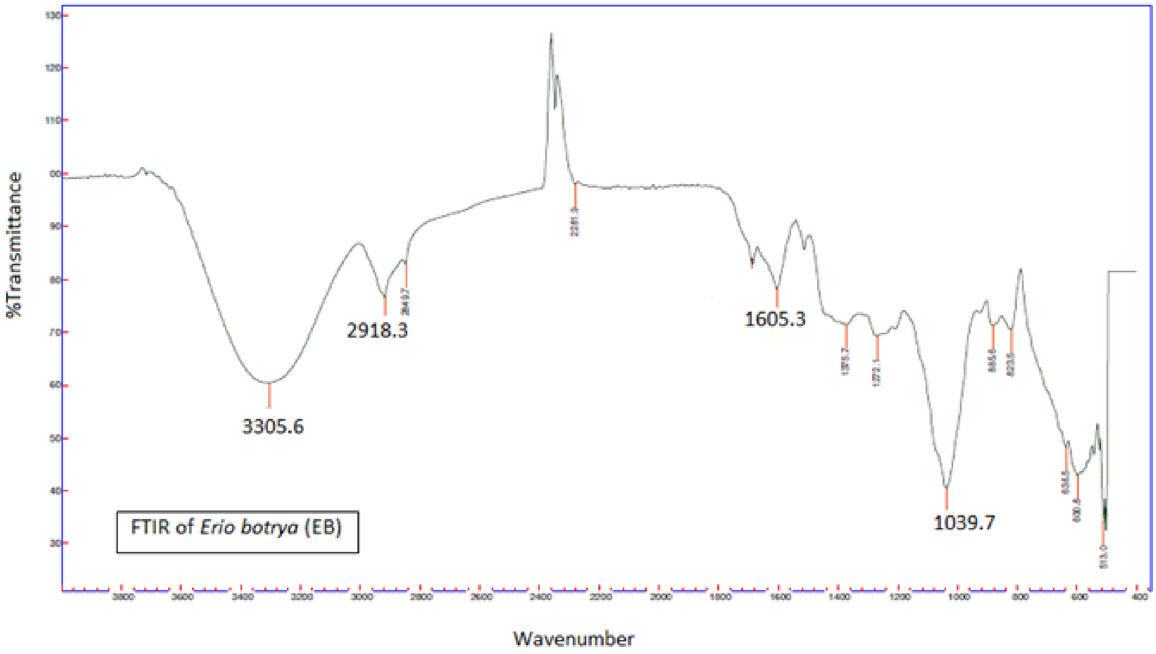

Figure 7. IR spectrum for Eriobotrya leaf extract.

It was reported that [20] EB leaf extract contains a substance known as Amygdalin (Vitamin B-17), Figure 8. The expected spectrum band of the hydrolyzed form of this chemical compound is in a good agreement with that obtained from FTIR spectroscopy measurement.

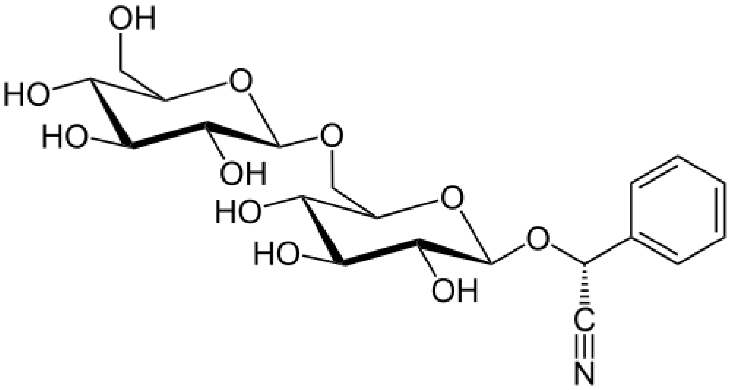

Figure 8. The chemical structure of Amygdalin

3.4. *Application of Temkin adsorption model*

Attempt was made to fit ($\theta = \eta/100$) values to Temkin model that is given by: [21]

$$\theta = 1/f \ln K.C$$

where f is the factor of energetic homogeneity, the heterogeneous factor of the metal surface describing the molecular interactions in the adsorption layer [22]. if f > 0, mutual repulsion of molecules occurs and if $f < 0$ attraction takes place [23]. The parameters obtained from linear fitting of Temkin models for EB leaf extracts in 0.5M HCl and 0.5M H_2SO_4 at 30°C are depicted in Table 3. The values of correlation coefficient (R^2) were used to judge the best-fit isotherm. In the present study, the strong correlation ($R^2 > 0.99$) suggests that the adsorption of EB on the surface obeyed the used model. The efficiency of EB plant leaf extract is essentially a function of the magnitude of its binding constant K, large values of K mean better and stronger interaction, whereas small values of K mean that the interaction between the inhibitor molecules and the metal is weaker [24]. Hence, according to the numerical values of K obtained from the model, the inhibition efficiency of EB leaf extracts in 0.5M HCl is greater than in 0.5M H_2SO_4. The positive values of the adsorption parameter (f), obtained from Temkin isotherm; suggest the occurrence of mutual repulsion of the active chemical ingredient of EB leaf extract [25, 26].

Table 3. Linear fitting parameters of EB leaf extract according to Temkin model in 0.5M HCland 0.5M H_2SO_4at 30°C

Solution	**Temkin**		
	K	f	R^2
0.5M HCl	62.44	5.07	0.99
0.5M H_2SO_4	50.12	5.75	0.99

3.5. Effect of temperature

Temperature is an important kinetic factor that influences the corrosion rate of metal and modifies the adsorption of inhibitor on electrode surface. Figure 9 shows the potentiodynamic polarization curves for steel in in the absence and presence of 0.8g.L^{-1} EB leaf extract in 0.5M HCl at different temperature.

As seen, increasing temperature, enhance both anodic metal dissolution and cathodic hydrogen evolution processes. This behavior could be interpreted on the basis that the increase in temperature results in desorption of the inhibitor from the surface of mild steel [27].

Figure 10 shows Nyquist Impedance plots for mild steel in 0.5M HCl in the presence of 0.80g.L^{1}*EB* leaf extract at different temperatures. As seen, increasing the temperature decreases the size of the depressed semicircles indicating increase of the corrosion rate (reciprocal of the charge transfer resistance), which may be attributed to the desorption of the adsorbed film.

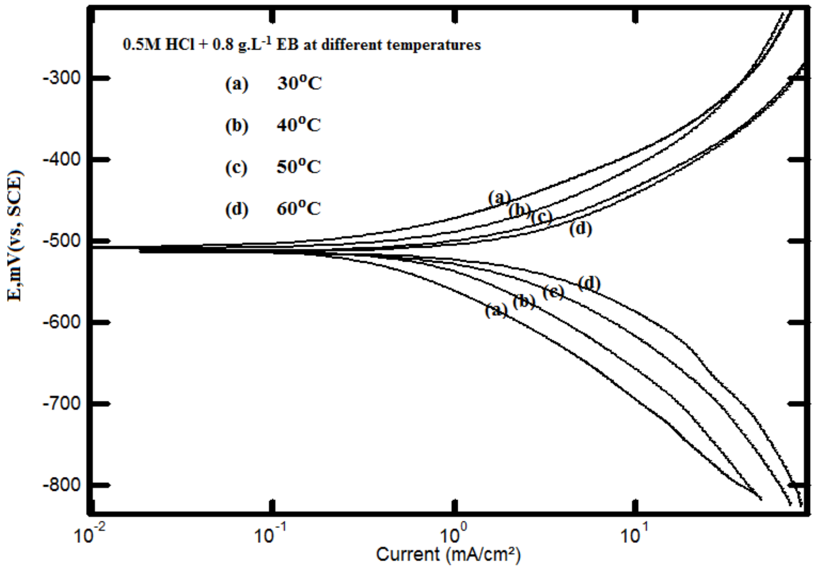

Figure 9. Potentiodynamic polarization curves for mild steel in 0.5M HCl in the presence of 0.80g.L^{-1} EB leaf extract at different temperatures

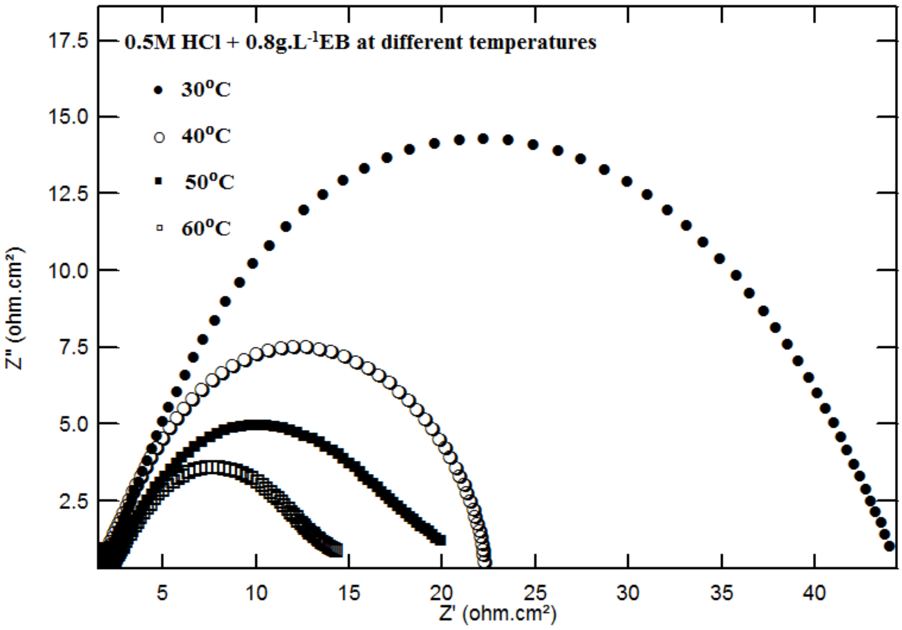

Figure 10. Nyquist Impedance plots for mild steel in 0.5M HClin the presence of 0.80g.L^{-1}*EB*leaf extract at different temperatures.

Similar observations were recorded (not shown) from the measurements of potentiodynamic polarization curves and electrochemical impedance spectroscopy for recorded for mild steel in 0.5M H_2SO_4 in the presence of 0.20g.L^{-1}.

The values of activation energy E_a and activation enthalpy ΔH^*_a were estimated using Arrhenius equation and transition state equation [28]:

$$\ln\upsilon = \ln A - (E_a/RT)$$

Where υ is the corrosion rate and is taken as reciprocal of the charge transfer resistance (R_{ct}) obtained from the Nyquist plots, E_a is apparent activation energy, A; the pre-exponential factor, and R is the universal gas constant. An alternative formulation of the Arrhenius equation is the transition state equation [28]:

$\upsilon=(RT/Nh)\exp((\Delta S^*/R)\exp(-\Delta H_*/RT)$

Where ΔH_* is the apparent enthalpy of activation, ΔS^* is the apparent entropy of activation, h is the Planck's constant and N is the Avogadro`s number, respectively.

This binding constant K is related to the standard free energy of adsorption (ΔG_{ads}), with the following equation [25].

$K_{ads} = 1/55.5\ e^{(-\Delta Gads/RT)}$

where R is the molar gas constant, T is the absolute temperature in Kelvin and 55.5 is the concentration of water in solution expressed in molar.

The activation parameters for steel in 0.5M HCl and 0.5M H_2SO_4 in the absence and presence of 0.8 and 0.2 $g.L^{-1}$ of EB leaf extracts were obtained from the linear square fitting of log (ν) and log(ν/T) data vs. (1/T), as shown in Figures 11 and 12 respectively. The calculated values for the activation parameters together with ΔG_{ads} are given in Table 4.

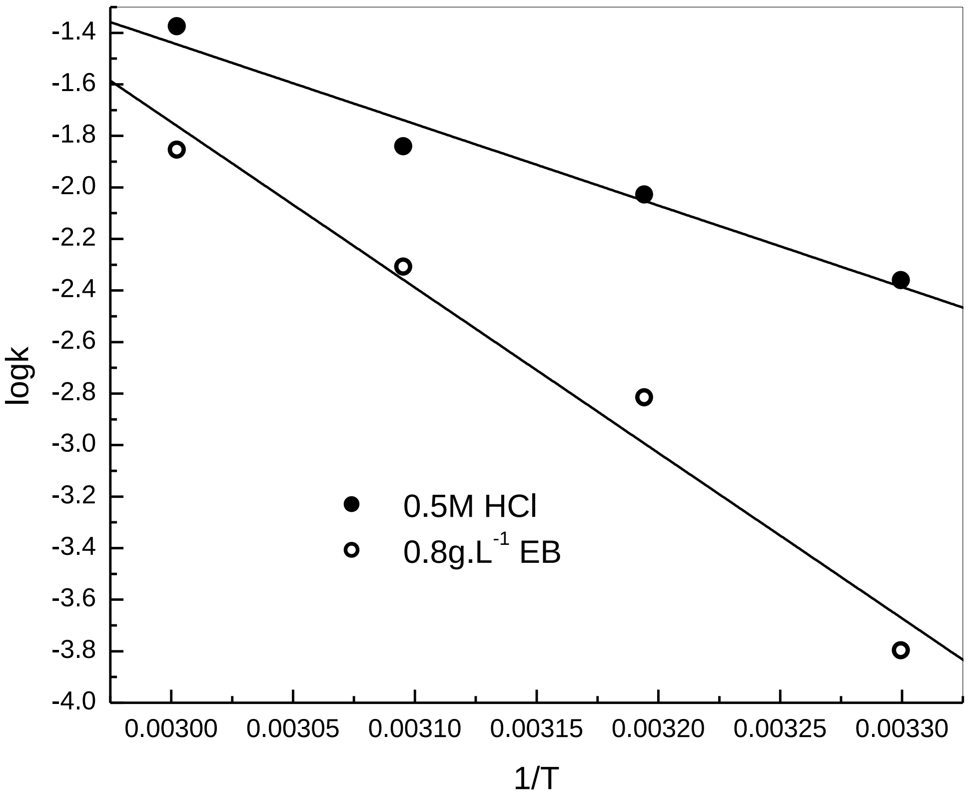

Figure 11. Variation of log (k) vs. 1/T of mild steel in 0.5M HCl in the absence and presence of 0.80 $g.L^{-1}$ EB leaf Extracts.

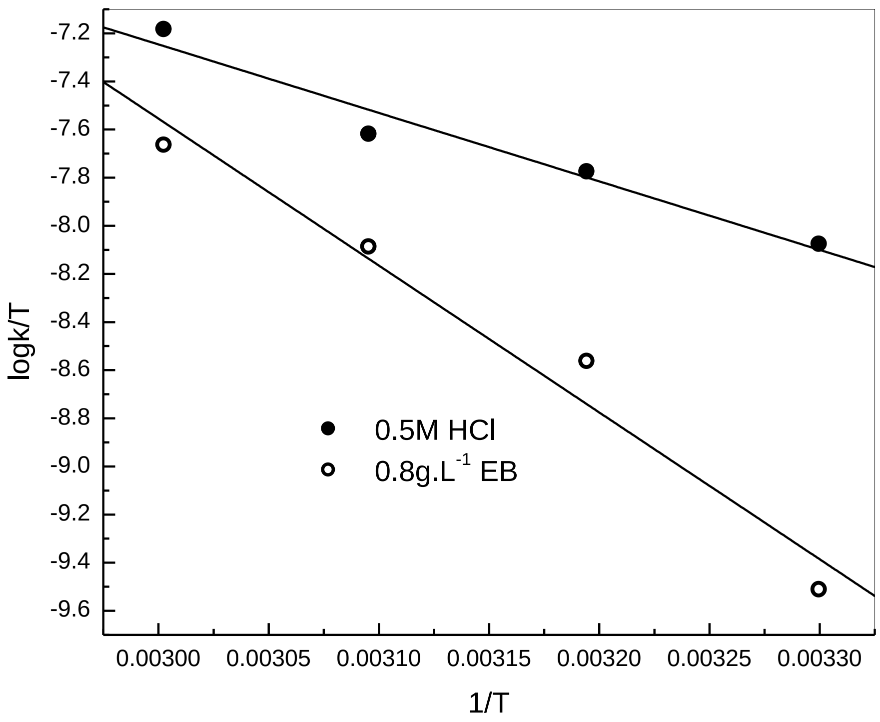

Figure 12. Variation of log (k/T) vs. 1/T of mild steel in 0.5M HCl in the absence andpresence of 0.80 g.L^{-1} EB leaf Extracts.

Table 4. The activation parameters of mild steel in 0.5M HCl and 0.5M H_2SO_4 in the absence and presence of 0.80 and 0.2 g.L^{-1} *EB* leaf Extracts respectively.

Acid Solution	Plant leaf extract	E_a kJ.mol^{-1}	ΔH* kJ.mol^{-1}	ΔS* J.mol^{-1}.K^{-1}	ΔG_{ads} kJ.mol^{-1}
0.5 M HCl	-	31.79	29.16	-172.59	-
	EB	53.37	50.07	-100.17	-14.09
0.5M H_2SO_4	-	13.86	11.23	-57.25	-
	EB	28.45	25.80	-184.18	-12.95

Inspection of the data show that the values of E_a and ΔH* in the presence of the leaf extract are higher than those of pure acid indicating geometric blocking effect of adsorbed chemical species of the extract on the metal surface [29]. In addition, their values are higher in HCl than H_2SO_4 suggesting that the energy barrier between the reactants and the activated complex depends on the type of the used acid. Moreover, the average difference values of the (E_a -ΔH*) are 2.63, 3.3, 2.63 and 2.65 kJ/mol which are approximately equal to the average value of RT (2.63 kJ/mol) at 30°C. This indicates that the corrosion process is a unimolecular reaction as it is characterized by the following equation [30]:

$E_a - \Delta H^* = RT$.

The positive values of ΔH* indicate that the formation of the activated complex is endothermic process. The negative value of ΔS* implies that the activated complex represents an association rather than a dissociation step. This means that a decrease in disordering takes place on going from reactants to the activated complex [31-33].

The negative values of the ΔG_{ads} reflect the spontaneity of the adsorption process of EB leaf extract and the stability of the adsorbed layers on the mild steel surface in both acidic solutions. Generally, values of ΔG_{ads} up to -20 kJ.mol^{-1} are consistent with electrostatic interactions between the charged molecules and the metal (physisorption mechanism), while those around -40kJ moL^{-1} or more negative are associated with chemisorption as a result of sharing or transfer of electron pair or π electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption mechanism) [25, 34- 35]. The obtained data indicate that the adsorption of EB leaf extract on metal surface is physisorption rather than chemisorption.

4. CONCLUSION

Electrochemical measurements indicated that the extract acts as mixed type inhibitor in 0.5M HCl and anodic type in 0.5M H_2SO_4. The adsorption process is spontaneous and obeys Temkin model. Corrosion inhibition of EB leaf extract is mainly due to the physical adsorption of the protonated chemical constituents of the extract on the mild steel surface. EB leaf extracts are more effective in HCl because Cl^- ion specifically adsorbed on the steel surface leading to reversal of charge. The resultant negatively charged surface attracts the positive moiety of the extract forming a barrier to the aggressive acid solution. On the other hand, the iron surface in H_2SO_4, where little specific adsorption of the anion occurs, is positively charged. Hence, the positively charged cationic moieties of EB extract are hardly adsorbed on the surface.

ACKNOWLEDGEMENT
This work is financially supported by National Council for Scientific Research (CNRS) Lebanon, reference number (05-13-12).

References

1. P. Mourya, S. Banerjee, R.B. Rastogi, M.M. Singh, *Ind. Eng. Chem*. 52 (2013) 12733–12747.
2. S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, *Corros. Sci*. 53 (2011) 1484–1488.
3. E.E. Oguzie, *Corros. Sci.* 50 (2008) 2993–2998.
4. V.V. Torres, R.S. Amado, C.F. de Sá, T.L. Fernandez, C.A.D.S. Riehl, A.G. Torres, E. D'Elia, *Corros. Sci*. 53 (2011) 2385–2392.
5. H. Bentrah, Y. Rahali, A. Chala, *Corros. Sci.* 82 (2014) 426–431.
6. A. Ostovari, S.M. Hoseinieh, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, *Corros. Sci*. 51 (2009) 1935–1949.
7. M. Lebrini, F. Robert, A. Lecante, C. Roos, *Corros. Sci*. 53 (2011) 687–695.
8. S.D. Deng, X.H. Li, *Corros. Sci*. 55 (2012) 407–415.
9. P.B. Raja, A.K. Qureshi, A.A. Rahim, H. Osman, K. Awang, *Corros. Sci*. 69 (2013) 292–301.
10. C. Cao, Corros.Sci. 38 (1996) 2073–2082.

11. A.M. Abdel-Gaber, N. Khalil and A. Abou El-Fetouh, *Anti Corros. Method M.*, 50(2003)442-447.
12. F.M. Reis, H.G. de Melo, I. Costa, *Electrochim. Acta* 51 (2006) 1780–1788.
13. M. Lebrini, M. Legrenee, H. Vezin, M. Traisnel, F. Bentiss, *Corros. Sci*. 49(2007) 2254–2269.
14. D.K. Yadav, B. Maiti, M.A. Quraishi, *Corros. Sci*. 52 (2010) 3586–3598.
15. S. Yuan, S.O. Pehkonen, B. Liang, Y.P. Ting, K.G. Neoh, E.T. Kang, *Corros. Sci*. 53 (2011) 2738–2747.
16. H. Ma, X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, L. Niu, *Corros. Sci*. 42(2000) 1669–1683.
17. S.K. Singh, S.P. Tambe, G. Gunasekaran, V.S. Raja, D. Kumar, *Corros. Sci*. 51(2009) 595–601.
18. F. Bentiss, M. Lagrenee , M. Traisnel, J.C. Hornez; *Corros. Sci*. 41(1999)789–803.
19. A. Popova, E. Sokolova, S. Raicheva, M. Christov; *Corros. Sci*. 45(2003)33–58.
20. Hamada, Atsuhide, S. Yoshioka, D. Takuma, J. Yokota, T. Cui, M. Kusunose, M. Miyamura, S. Kyotani, and Y. Nishioka., *Biol Pharm Bull* 27 (2004) 1961-964.
21. M.I.Temkin, *J. Phys. Chem*., 14(1940)1153.
22. N.O.Obi-Egbedi, K.E.Essien and I.B.Obot, *J. Comp. Method Mol. Design*, 1(2011) 26-43.
23. N. J. N.Nnaji, N.O.Obi-Egbedi and J.U.Ani, *J. Sci. and Ind Studies*, 9(2011) 26-32
24. B.A. Abd-El-Nabey, A.M. Abdel-Gaber, G.Y.Elawady and S. El-Housseiny, *Int. J. Electrochem. Sci*., 7(2012) 7823 – 7839.
25. H. Ashassi-Sorkhabi, B.Shaabani, B.Aligholipour and D.Seifzadeh, *Appl. Surf. Sci.* 252(2006)4039-4047.
26. A.M. Abdel-Gaber, M.S. Masoud, E.A. Khalil, E.E. Shehata, *Corros. Sci*.51 (2009) 3021–3024.
27. Sethuraman, M.G., Aishwarya, V., Kamal, C., Edison, T.J.I., *Arab. J. Chem*. http://dx.doi.org/10.1016/j.arabjc.2012.10.01.
28. X.H. Li, S.D. Deng, H. Fu, *Corros. Sci*. 62 (2012) 163–175.
29. Tebbji, K., Faska, N., Tounsi, A., Oudda, H., Benkaddour, M.,Hammouti, B., *Mater. Chem.Phys*. 106(2007) 260–267.
30. K.J. Laidler, Reaction kinetics, vol. 1, first ed., Pergamon Press, New York, 1963.
31. O.R. Khalifa&S.M.Abdallah, *Port Electrochim Acta*, 29(2011) 47-56.
32. G.Cristofari, M. Znini, L. Majidi, A. Bouyanzer, S.S. Al-Deyab, J. Paolini , B. Hammouti and J. Costa, *Int. J. Electrochem. Sci.*, 6(2011) 6699 – 6717.
33. D. Ben Hmamou, R. Salghi, H. Zarrok,Zarrouk, Abdelkader ,B. Hammouti, M. El Hezzat,& M.Bouachrine, *Adv Mater Corros*; 1(2012)36-42.
34. L.Wang, M.Lu Xu, S.K. Rasmussen and M.H.Wang, *Carbohydr. Res.*, 346 (2011)1212–1216.
35. B.Berka-Zougali, M.A.Ferhat, A. Hassani, F. Chemat, and K.S.Allaf, *Int J Mol Sci.*, 13(2012)4673–4695.