



***Malvasylvestris* Flower Extracts as Green Corrosion Inhibitor for Carbon Steel in HCl Solution**

Razieh Salahandish¹, Ali Ghaffarinejad^{1,2*}, Ali Moradpour¹

¹Research Laboratory of Real Samples Analysis, Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran

²Electroanalytical Chemistry Research Center, Iran University of Science and Technology, Tehran, Iran

(Received 29 May 2016; Final version received 20 Jul. 2016)

Abstract

In this study, *Malvasylvestris* flower extract (MFE) was used as a corrosion inhibitor for carbon steel in 1 M HCl solution. *Malvasylvestris* extract was analyzed by gas chromatography coupled with a mass spectrometry detector (GC-MS). Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies revealed that the inhibition efficiency increases with increasing MFE concentration. Scanning electron microscopy (SEM) studies performed at various contact times of alloy with acid solution showed that the corrosion rate is reduced considerably in the presence of bioinhibitor. Corrosion studies at various temperatures (298 –338 K) showed that even at temperatures higher than 298 K the inhibition efficiency is good (>91%). Thermodynamic test results indicate that the MFE adsorption on the metal surface occurs by a chemisorption mechanism, and its adsorption isotherm is Langmuir.

Keywords: Carbon steel, *Malvasylvestris* flower, Bioinhibitor, EIS, Polarization.

Introduction

Metal corrosion remains a world-wide scientific problem as it affects the metallurgical, chemical and oil industries [1]. Steel and steel-based alloys of different grades steel are the major construction materials used extensively in chemical and its allied industries for

handling acid, alkali and salt solutions[2, 3]. Their excellent mechanical properties and cost effectiveness make them suitable construction materials. Carbon steel, however easily undergoes corrosion in various environmental conditions especially in acidic media [4]. Acid solutions are generally used for the removal

*Corresponding author: Ali Ghaffarinejad, Research Laboratory of Real Samples Analysis, Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran. Tel.: +98-21-77240516; Fax: +98-21-77491204. E-Mail: Ghaffarinejad@iust.ac.ir.

of undesirable scale and rust in several industrial processes. Hydrochloric acid is widely used in the pickling processes of metals [5, 6]. Hazardous effects of some synthetic corrosion inhibitors have motivated scientists to use products of natural origin for material preservation: various plant extracts have been used as corrosion inhibitors [7], also referred to as eco-friendly or green corrosion inhibitors [8].

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [4]. The successful application of naturally occurring substances as metal corrosion inhibitor in acidic and alkaline environment have been reported by several researchers [9-16]. Several recent studies have reported the application of biomaterials as green corrosion inhibitors for carbon steel in acidic media. Some examples include *Palicourea guianensis* [3], *Foeniculum Vulgare* [17], *Oxandraasbeckii* [18], *thioureas* [19], *watermelon* rind [20], *Punicagranatum* peel [21], *Guar* gum [22], *Neolamarckiacadamba* [23] and *verbena* essential oil [15].

In the current study MFE was employed for the first time as a green corrosion inhibitor for carbon steel in HCl solution. The low price of the aforementioned flower, its considerable growth as a weed in most parts of the world and its much better inhibition efficiency compared to leave extracts of the same plant [7] make it a suitable choice as a green corrosion inhibitor

for carbon steel.

Experimental

Malvasylvestris extract preparation

The *Malvasylvestris* flowers were dried at room temperature for 24 h, and then screened with 30-mesh size. 10 g of flower powder was packed in filter paper and put in Soxhlet extractor, then 125 mL of ethanol was poured into the flask, the reflux and extraction was then performed at 100°C for 24 h. The resulting solution composed of the extracted materials in ethanol was then used as inhibitor.

Materials and methods

An analytical reagent-grade HCl was used for preparing acid solutions. 1 μ L of the *Malvasylvestris* extract was analyzed by GC-MS using Perkin Elmer GC Clarus 680 equipped with a Perkin Elmer Clarus SQ8 S mass spectrometer (U.S.A.). The applied column was Elite-5MS (0.25 μ m film thickness). The oven temperature was programmed to hold at 40 °C ramped at 25 °C min⁻¹ until 300 °C. The carrier gas was He (99.999%) and the injector and detector temperature were adjusted to 280 °C and 300 °C, respectively.

All electrochemical studies were performed using a Potentiostat/Galvanostat model of Autolab PGSTAT 30 (Echo chemie, B. V., Netherlands). The software of this device was Nova version 1.7.8. The experiments

were carried out using a conventional three-electrode system with Ag|AgCl|3 M KCl as the reference, and a Pt rod as the counter electrode. Working electrodes were cut from a C75S carbon steel sheet (Mn: 0.700, S: 0.017, C: 0.689 and Si: 0.191, P: 0.026, Cr: 0.242, Cu: 0.019 and Fe.) with a surface area of 1 cm². Before each electrochemical measurement the electrode surface was cleaned with acetone and then washed with deionized water. Potentiodynamic polarization curves were obtained in 1 M HCl in different concentrations (5 – 20% v/v) of MFE, and at various temperatures in the absence and presence of MFE. Polarization curves were obtained in the potential range of -1 to 0 V with the scan rate of 0.5 mV s⁻¹. EIS measurements were accomplished in the frequency range of 10⁻² – 10⁵ Hz, and the potential amplitude was 14 mV around the E_{corr} . In order to study carbon steel surface morphology, scanning electron microscopy

(SEM) images before and after addition of inhibitor were taken by SEM instrument model VEGA//TESCAN (Czech Republic). For microscopic observation of the alloy surface, the carbon steel was dipped in 1 M HCl for 15, 30 and 60 min contact times in the presence and absence of bioinhibitor. Then after each contact time the surface morphology was observed by SEM.

Results and discussion

GC-MS analysis

The composition of the *Malva* extract was analyzed by GC-MS and its main components were identified by matching the obtained spectra with the instrument database. Table 1 summarizes the results of this analysis. According to this table the active ingredient of this plant includes organic materials that like most natural corrosion inhibitor molecules have functional groups containing oxygen and nitrogen.

Table 1. Characterization of the most abundant chromatographic peaks of MFE.

Number	1	2	3	4
Retention time(min)	1.374	1.379	1.444	1.519
Name	3-(Dimethylamino)-4-sydnone	DL-3-Aminobutyric acid	Methyltartronic acid	Oxirane, (fluoromethyl)
Formula	$C_5H_9N_4O_3^+$	$C_4H_9NO_2$	$C_4H_6O_5$	C_3H_5FO
2D structure				

Investigation of MFE concentration effect by Tafel and EIS plots

Electrochemical parameters including corrosion current density (j_{corr}), corrosion potential (E_{corr}) and cathodic Tafel slopes (β_c) were obtained from the polarization curves (Figure 1) and are given in Table 2. The

inhibition efficiency ($IE\%$) was defined as:

$$IE\% = \frac{j_{co}^{\circ} - j_{co}}{j_{co}^{\circ}} \times 100 \quad (1)$$

where j_{corr}° and j_{corr} are the corrosion current density values in the absence and presence of inhibitor, respectively.

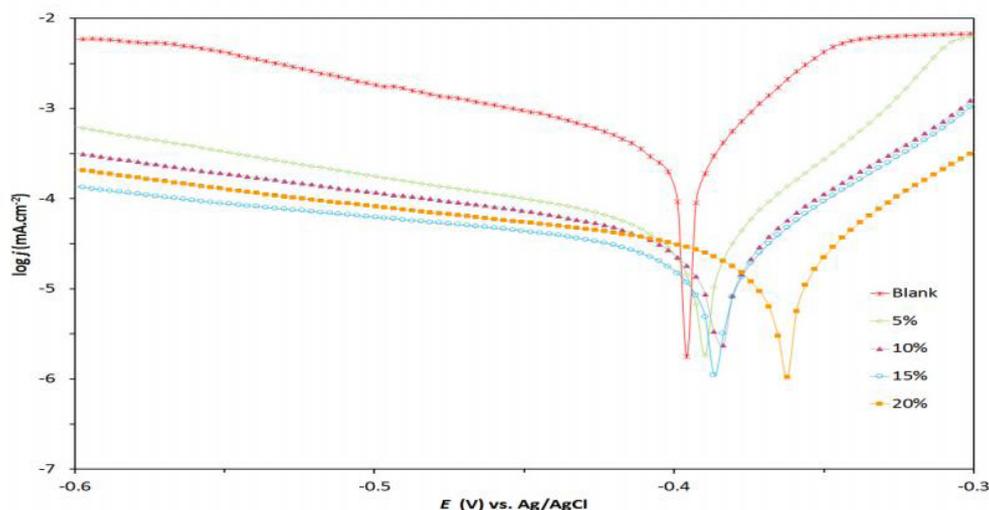


Figure 1. Potentiodynamic polarization curves for carbon steel in 1 M HCl containing different concentrations of inhibitor (Scan rate 0.5 mV s^{-1}).

Table 2. Potentiodynamic electrochemical parameters obtained for carbon steel in 1M HCl containing different concentrations of MFE.

MFE Conc. (v/v%)	E_{corr} (mV)	j_{corr} ($\mu\text{A.cm}^{-2}$)	$-\beta_c$ (mV.dec^{-1})	IE (%)
0	-392	312	36.9	-
5	-390	40	39.7	87.2
10	-386	20	49.8	93.6
15	-387	17	49.1	94.6
20	-363	16	47.1	94.9

These results indicate that in the presence of MFE, E_{corr} shifts to more positive potentials and the value of j_{corr} decreases. Also both the anodic and cathodic current densities reduce, which indicates the suppression of both the anodic and cathodic reactions by MEF, which may be due to the adsorption of the inhibitor on the alloy surface. This suggests that MFE acts as a mixed-type corrosion inhibitor for carbon steel in 1 M HCl solution [15]. According to the considerable shift of E_{corr} , it can be concluded that the inhibition effect is mainly due to the blocking of the active sites [15]. Data

presented in Table 2 indicate that increasing in MFE concentration lead to IE% increasing. Fig. 2 shows the Nyquist plots obtained from impedance measurements for carbon steel in 1M HCl solution in the absence and presence of different concentrations of MFE. The polarization resistance (R_p) and constant phase element (CPE) values were obtained after data fitting with the appropriate equivalent electrical circuits (inset of Figure 2). The CPE is used since this interface does not show ideal capacitor behavior.

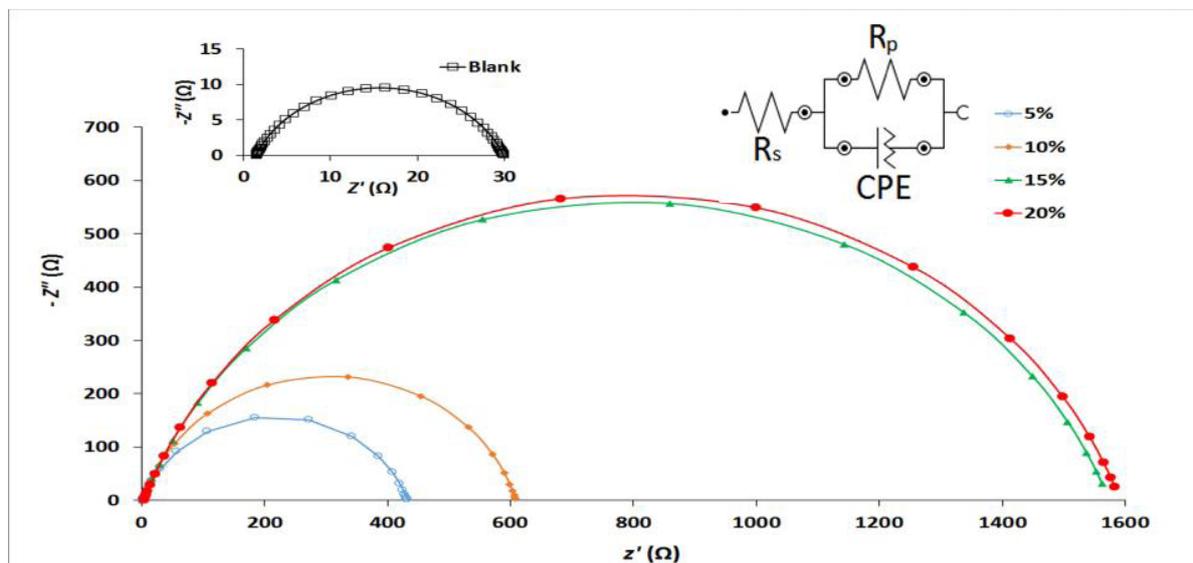


Figure 2. Nyquist plots for carbon steel in 1 M HCl in the absence and presence of different concentrations of MFE, **Inset:** Equivalent electrical circuit for carbon steel in the presence and absence of inhibitor (R_s : ohmic resistance of the solution, R_p : polarization resistance and CPE : constant phase element).

In this study, inhibition efficiency ($IE\%$) was calculated with equation 2:

$$IE\% = \frac{R_p - R_p^0}{R_p} \times 100$$

In which R_p^0 and R_p represent the polarization resistance in the absence and presence of MFE respectively. Table 3 summarizes the electrochemical parameters obtained from EIS data. According to Figure 2 and Table 3, R_p of the carbon steel in the presence of MFE increases considerably, and the corrosion resistance increases by increasing the inhibitor concentration up to 20%. According to the Nyquist plots, by increasing the concentration of inhibitor from 15 – 20 % increasing of R_p is moderate, therefore concentrations greater than 20% was not used. The increase in R_p values by increasing inhibitor concentrations may suggest the formation of an adsorbing

layer on the electrode surface. This layer is a barrier to mass and charge transfer [15]. The single semicircle in Figure 2 indicates that charge transfer occurs with one pathway [15]. Also this figure reveals that addition of inhibitor increases the semicircle diameter of the Nyquist plots without affecting their characteristic features. This means that the inhibition action of these inhibitors is due to their adsorption on the metal surface without altering the corrosion mechanism [24]. The decrease in the CPE values can be attributed to the adsorption of inhibitor forming a protective adsorption layer [25].

Table 3. Corrosion parameters obtained by impedance measurements for carbon steel in 1 M HCl (in presence and absence of various concentrations of MFE).

	MFE Conc. (v/v%)	$R_s(\Omega.cm^{-2})$	$R_p(\Omega.cm^{-2})$	$CPE(\mu F.cm^{-2})$	$IE(\%)$
Blank	0	1.41	28.52	356	-
MFE	5	1.66	430.88	69	93.3
	10	1.85	606.68	31	95.2
	15	2.47	1572.50	43	98.2
	20	3.45	1588.50	33	98.2

Challouf et al. [7] have recently applied *Malvasylvestris* leave extracts as mild steel inhibitor in NaCl 0.5 M with 54.5% inhibition efficiency. Considering the more corrosive solution (1 M HCl) used in our study, the inhibition efficiency of the MFE is much better (95%) compared to the results of the

mentioned study. Table 4 provides a detailed comparison among some recently reported articles about the application of bioinhibitor for carbon steel corrosion protection in 1 M HCl. Table 4 shows improved $IE(\%)$ results compared to those gained from other studies.

Table 4. Comparing parameters of inhibition for carbon steel corrosion in 1 M HCl at this work with several recently published reports.

Bioinhibitor	$j_{corr}(\mu A.cm^{-2})$	$E_{corr}(mV)$	$IE(\%)$	Reference
<i>Palicourea guianensis</i>	23	-466	90	[3]
<i>Aloes</i>	286	-487	70.79	[5]
<i>Aquilaria Crassna</i> Leaves	316	-464	60	[10]
<i>verbena</i>	16	-541	85.5	[15]
<i>Foeniculum Vulgare</i>	161	-472	77	[17]
<i>Oxandraasbeckii</i>	27	-472	88	[18]
<i>watermelon rind</i>	45.5	-504	79.9	[20]
<i>Neolamarckiacadamba</i> Leaves	229	-450	88	[23]
This work	16	-363	94.9	-

Surface morphology study by SEM

The surface morphologies of carbon steel at various times are shown in Figure 3. As this figure shows, in the absence of MFE

the surface is corroded extremely, but in the presence of bioinhibitor, corrosion of the alloy decreases considerably.

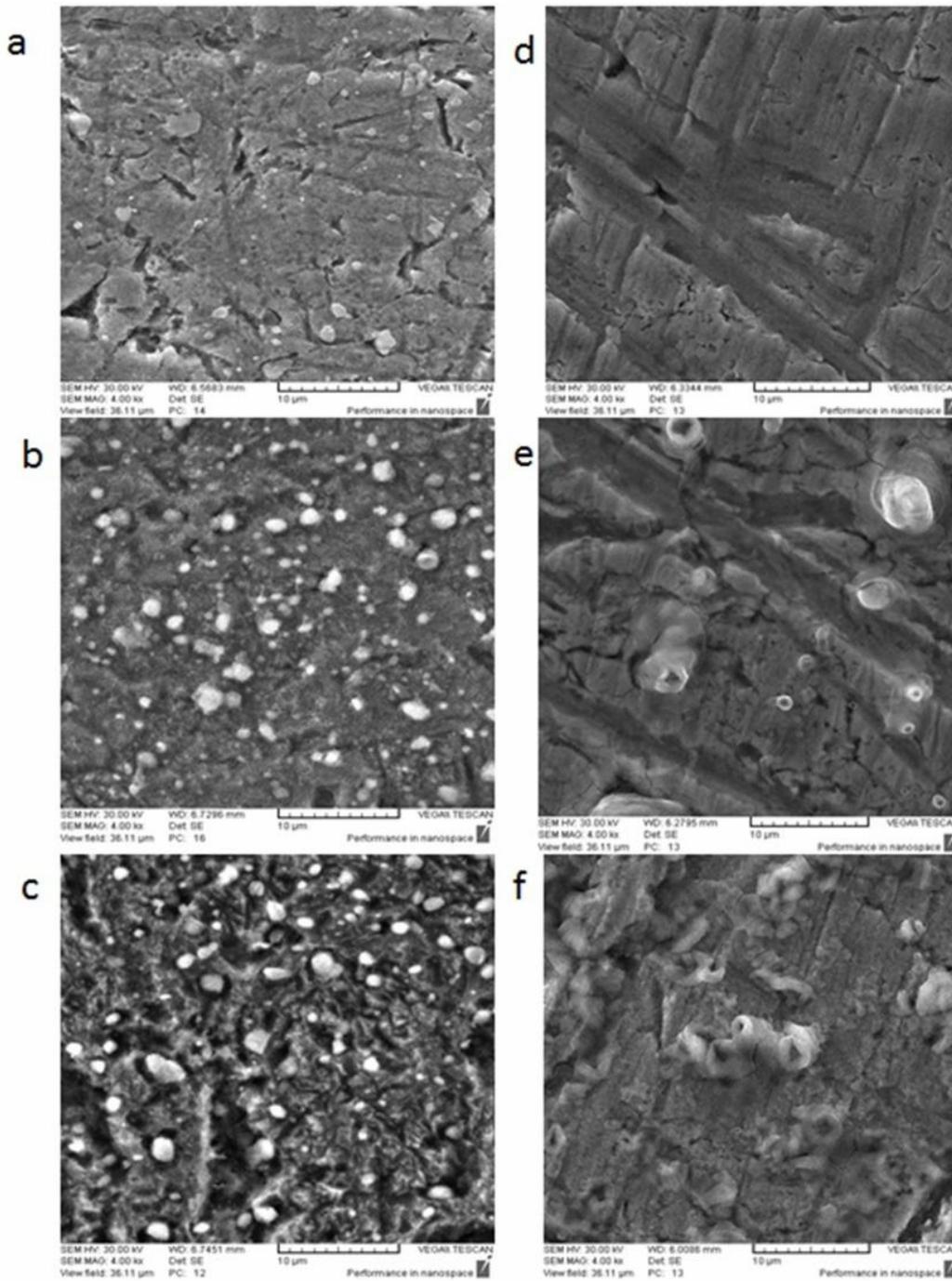


Figure 3. SEM images of carbon steel surface at various contact time with 1 M HCl solution in the absence (a: 15, b: 30 and c: 60 min) and presence (d: 15, e: 30 and f: 60 min) of MFE.

Effect of temperature

Temperature is usually an important parameter in metal corrosion. The corrosion rate in acid solutions, for example, increases exponentially

along with increasing temperature, because the hydrogen evolution over potential decreases [26]. The effect of temperature on the corrosion rate of carbon steel was investigated in 1 M

HCl in the absence and presence of 20% MFE. In this study polarization curves at various temperatures (298, 308, 318, 328 and 338 K) with the scan rate of 0.5 mV s^{-1} were obtained in the absence (Fig. 4) and presence of MFE

(Fig. 5). The value of j_{corr} was measured by extrapolation of the cathodic and anodic lines of the Tafel plot and their intersection with E_{corr} . Table 5 represents the j_{corr} , E_{corr} and cathodic Tafel slope (β_c) at these temperatures.

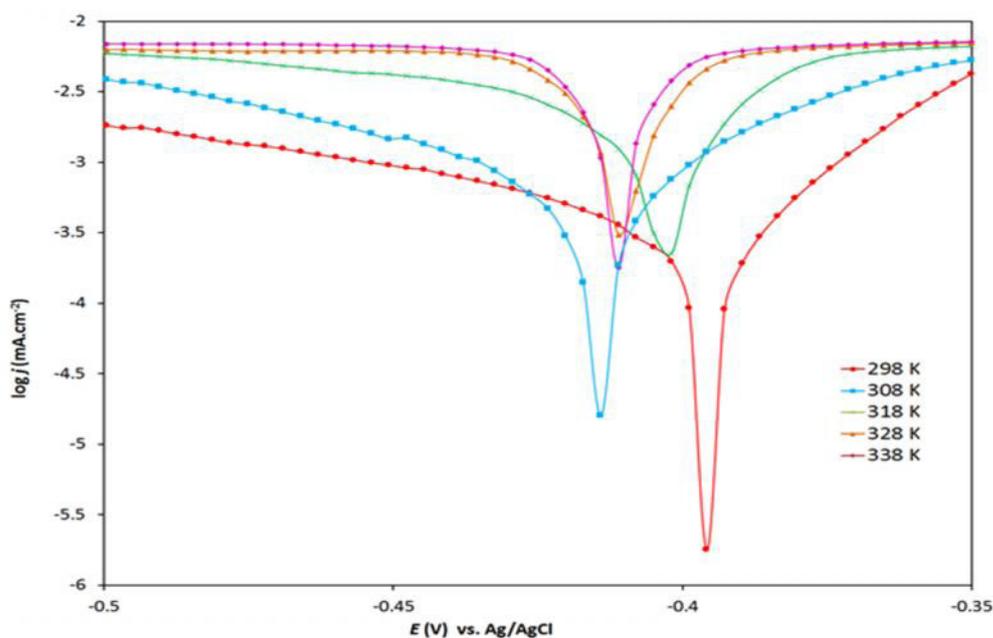


Figure 4. Effect of temperature on the cathodic and anodic polarization curves of carbon steel in 1 M HCl.

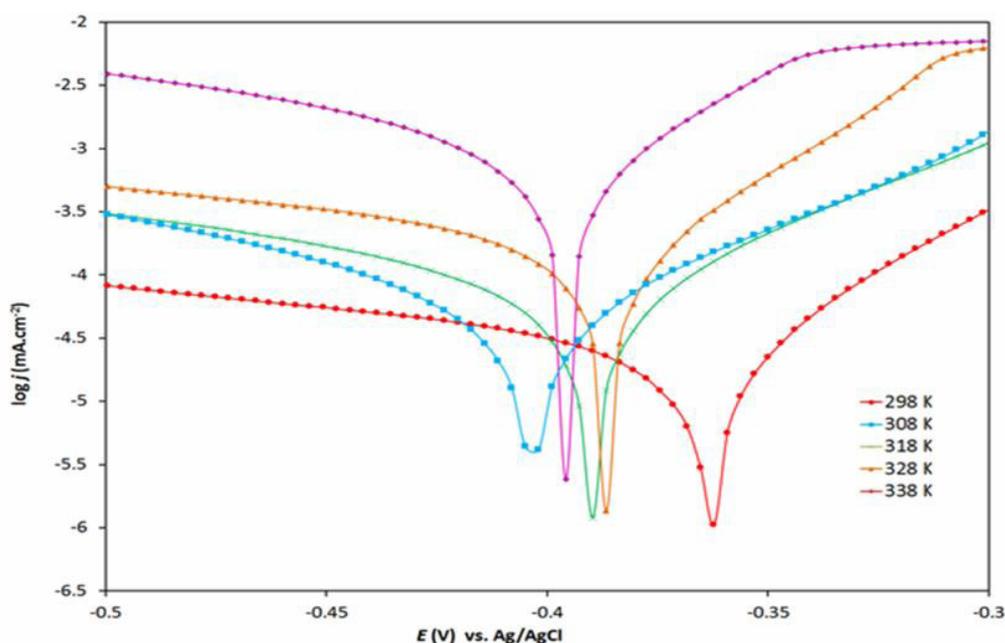


Figure 5. Effect of temperature on the cathodic and anodic polarization curves of carbon steel in 1 M HCl containing 20% v/v of MFE.

Table 5. Electrochemical data for carbon steel in 1 M HCl and in 1 M HCl containing 20% v/v of inhibitor at different temperatures, and the corresponding values of the corrosion inhibition efficiency.

	T (K)	E_{corr} (mV)	j_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$-\beta_c$ (mV.dec $^{-1}$)	IE (%)
Blank	298	-393	313	37	-
	308	-413	720	63	-
	318	-403	3302	139	-
	328	-405	6950	3978	-
	338	-406	7187	10246	-
Inhibitor	298	-364	16	47	94.8
	308	-402	59	71	91.8
	318	-384	82	69	97.5
	328	-379	112	46	98.4
	338	-392	395	43	94.5

According to this study the MFE reduces the corrosion rate considerably also at higher temperatures. Arrhenius-type dependence is observed between corrosion rate and temperature. The apparent activation energy (E_a) of the corrosion process can be calculated from the Arrhenius plots. The mechanism of inhibitor action can be concluded by comparing E_a measured both in the presence and absence of the inhibitor. According to the Arrhenius-type process, the values of activation energy (E_a) were calculated by the following equation:

$$j_{corr} = K \exp\left(-\frac{E_a}{R}\right) \quad (3)$$

Where K refers to the Arrhenius pre-exponential factor, T the absolute temperature and R the gas constant. The logarithm of the

corrosion rates was plotted vs. $1000/T$ (Fig. 6), which had a linear relation and the E_a value was obtained from the plot slopes. The E_a value in the absence of MFE was 73.09 kJ mol $^{-1}$, and 61.82 kJ mol $^{-1}$ in the presence of MFE. According to the previous reports the lower E_a value in the presence of inhibitor indicates chemisorption of the corrosion inhibitor [27, 28]. The iron in carbon steel, which is a transition metal with a vacant, low-energy electron orbital and the loosely bound electrons and heteroatoms in the MFE molecules support this proposition for the adsorption mechanism [27]: charge sharing or charge transfer from the MFE molecules to the carbon steel surface takes place to form a coordinate-type bond.

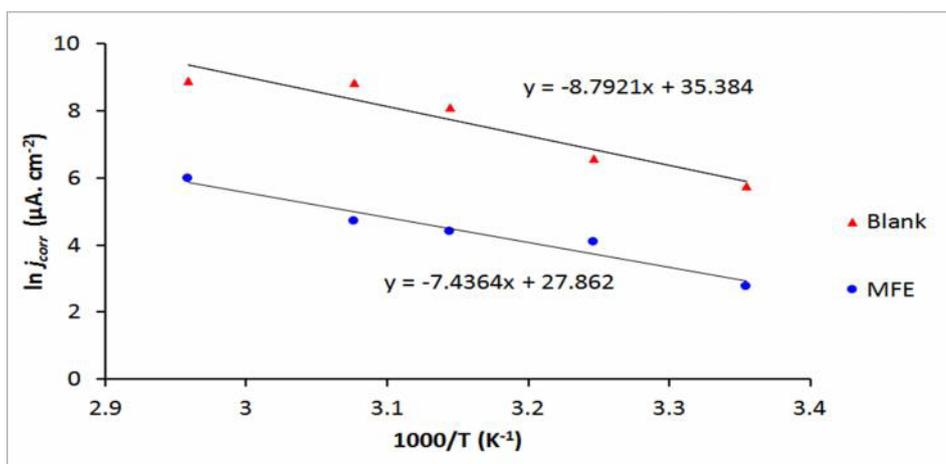


Fig. 6. Arrhenius plots of carbon steel in 1 M HCl in the presence and absence of 20% v/v MFE.

Adsorption isotherms

To investigate the inhibitor adsorption isotherms on the carbon steel surface, Langmuir, Temkin and Frumk in adsorption isotherms were evaluated according to the following equations:

Langmuir: $\theta/(1-\theta) = KC(4)$

Temkin: $\log(\theta/C) = \log K - g\theta(5)$

Frumkin: $\log(\theta/(1-\theta)C) = \log K + g\theta(6)$

Where θ represents the surface coverage, K the adsorption-desorption equilibrium constant, C the inhibitor concentration and g the adsorbate interaction parameter [27]. Considering that the double-layer capacitance is proportional

to the surface not covered by the adsorbed inhibitor, the fraction of the surface covered by inhibitor was determined according to the following equation[29]:

$$\theta = (1 - C_{dl}/C_{dl}^{\circ}) \times 100 \quad (7)$$

where C_{dl}° and C_{dl} represent the double-layer capacitance in the absence and presence of the corrosion inhibitor, respectively. The values of C_{dl}° , C_{dl} and θ are presented in Table 6. In order to find the best fitting adsorption isotherm, the relative surface coverage plots were obtained.

For the Langmuir (Figure 7A), Temkin (Fig. 7B) and Frumk in (Fig. 7C) isotherms, the r^2 values were 0.992, 0.961 and 0.819, respectively. According to these results the best fit is Langmuir isotherm.

Table 6. The values of C_{dl}° , C_{dl} and θ

MFE Conc. (%)	C_{dl}°	C_{dl}	θ	$\theta/(1-\theta)$	$\log(\theta/C)$	$\log(\theta/(1-\theta)C)$
0	356	-	-	-	-	-
5	-	69	0.81	4.26	3.21	1.93
10	-	31	0.87	6.69	2.94	1.83
15	-	43	0.88	8.34	2.77	1.69
20	-	33	0.91	10.11	2.66	1.70

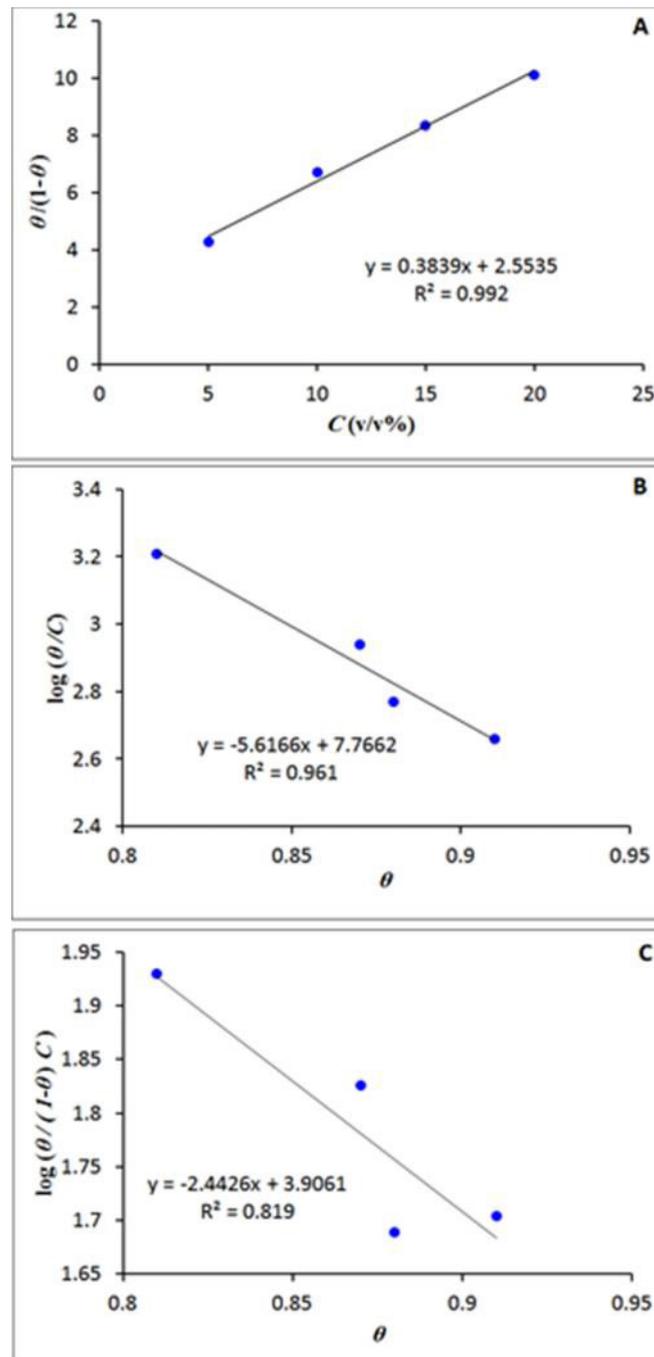


Figure 7. Langmuir (A), Temkin (B) and Frumkin (C) isotherms for the adsorption of MFE on the surface of carbon steel in 0.1 M HCl.

Conclusion

Results obtained from the experimental and theoretical data show that *Malvasylvestris* flower extract acts as an effective corrosion inhibitor for carbon steel in hydrochloric

acid. The corrosion process may be inhibited by chemisorption of the bioinhibitor molecules present in the extract on the carbon steel surface. Inhibition efficiency increases by increase in the concentration of the bioinhibitor. While

increasing in temperature in the absence of bioinhibitor lead to increase in corrosion rate, in the presence of bioinhibitor, the inhibition efficiency remains relatively constant at high level. EIS studies indicate that adsorption of bioinhibitor by the carbon steel surface causes increase in R_p and decrease in double-layer capacitance. The inhibitor efficiencies determined by electrochemical polarization and EIS methods are in good agreement.

Acknowledgments

We gratefully acknowledge the support of this work by the research councils of Iran University of Science and Technology.

References

- [1] M. Finšgar, J. Jackson, A review, *Corros. Sci.*, 86, 17 (2014).
- [2] E.A. Noor, A.H. Al-Moubaraki, *Int. J. Electrochem. Sci.*, 3, 806 (2008).
- [3] M. Lebrini, F. Robert, C. Roos, *Int. J. Electrochem. Sci.*, 6, 847 (2011).
- [4] K. Boumhara, F. Bentiss, M. Tabyaoui, J. Costa, J. Desjobert, A. Bellaouchou, A. Guenbour, B. Hammouti, S. Al-Deyab, *Int. J. Electrochem. Sci.*, 9, 1187 (2014).
- [5] H. Cang, Z. Fei, J. Shao, W. Shi, Q. Xu, *Int. J. Electrochem. Sci.*, 8, 720 (2013).
- [6] M.R. Singh, *Environments*, 4, 119 (2013).
- [7] H. Challouf, N. Souissi, M.B. Messaouda, E. Triki, R. Abidi, *Surface Engineering and Applied Electrochemistry*, 49, 320 (2013).
- [8] N. Patel, S. Jauhariand, G. Mehta, S. Al-Deyab, I. Warad, B. Hammouti, *Int. J. Electrochem. Sci.*, 8, 2635 (2013).
- [9] O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, R. Salghi, *J. Mater. Environ. Sci.*, 4, 127 (2013).
- [10] L. Helen, A. Rahim, B. Saad, M. Saleh, P.B. Raja, *Int. J. Electrochem. Sci.*, 9, 830 (2014).
- [11] M. Znini, M. Bouklah, L. Majidi, S. Kharchouf, A. Aouniti, A. Bouyanzer, B. Hammouti, J. Costa, S. Al-Deyab, *Int. J. Electrochem. Sci.*, 6, 691 (2011).
- [12] E. Ebenso, N. Eddy, A. Odiongenyi, *Afr. J. Pure Appl. Chem.*, 2, 107 (2008).
- [13] S. Africa, *Afr. J. Pure Appl. Chem.*, 2, 46 (2008).
- [14] S. Shivakumar, K. Mohana, *Adv. Appl. Sci. Res.*, 3, 3097 (2012).
- [15] D.B. Hmamou, R. Salghi, A. Zarrouk, H. Zarrouk, M. Errami, B. Hammouti, L. Afia, L. Bazzi, L. Bazzi, *Res. Chem. Intermed.*, 39, 973 (2013).
- [16] S. Rekkab, H. Zarrok, R. Salghi, A. Zarrouk, L. Bazzi, B. Hammouti, Z. Kabouche, R. Touzani, M. Zougagh, *J. Mater. Environ. Sci.*, 3, 613 (2012).
- [17] N. Lahhit, A. Bouyanzer, J. M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss and L. Majidi, *Port. Electrochim. Acta*, 29, 127 (2011).
- [18] M. Lebrini, F. Robert, A. Lecante, C. Roos, *Corros. Sci.*, 53, 687 (2011).

- [19] V.V. Torres, V.A. Rayol, M. Magalhães, G.M. Viana, L.C.S. Aguiar, S.P. Machado, H. Orofino, E. D'Elia, *Corros. Sci.*, 79, 108 (2014).
- [20] N.A. Odewunmi, S.A. Umoren, Z.M. Gasem, *J. Ind. Eng. Chem.*, 21, 239 (2015).
- [21] M. Behpour, S.M. Ghoreishi, M. Khayatkashani, N. Soltani, *Mater. Chem. Phys.*, 131, 621 (2012).
- [22] P. Roy, P. Karfa, U. Adhikari, D. Sukul, *Corros. Sci.*, 88, 246 (2014).
- [23] P.B. Raja, A.K. Qureshi, A. Abdul Rahim, H. Osman, K. Awang, *Corros. Sci.*, 69, 292 (2013).
- [24] I. Ahamad, R. Prasad, M.A. Quraishi, *Corros. Sci.*, 52, 933 (2010).
- [25] A.E.A.E.S. Fouda, A. Hussein, *J. Korean Chem. Soc.*, 56, 264 (2012).
- [26] A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.*, 45, 33 (2003).
- [27] F.S. de Souza, A. Spinelli, *Corros. Sci.*, 51, 642 (2009).
- [28] T. Szauer, A. Brandt, *Electrochim. Acta*, 26, 1253 (1981).
- [29] G. Lendvay-Györík, G. Mészáros, B. Lengyel, G. Lendvay, *Corros. Sci.*, 45, 1685 (2003).