International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/090307

Evaluation of Green Corrosion Inhibition by Extracts of *Citrus aurantium* Leaves Against Carbon Steel in 1 M HCl Medium Complemented with Quantum Chemical Assessment

Tayser S. Gaaz[1,], Rifat M. Dakhil[2], Dalia M. Jamil[3], Ahmed A. Al-Amiery[4], Abdul Amir Kadhum[5] and Mohd Takriff[5]*

[1]Al-Mussaib Technical College, Al-Furat Al-Awsat Technical University, 51006, Babylon, Iraq
[2]Technical College Basra, Southern Technical University, Iraq
[3]Chemistry Department, College f Science, Nahrain University, Baghdad 10001, Iraq
[4]Energy and Renewable Energies Technology Center, University of Technology, Baghdad 10001, Iraq
[5]Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia

Received: 6 Jul. 2020, Revised: 3 Aug. 2020, Accepted: 13 Aug. 2020.
Published online: 1 Sep. 2020.

Abstract: Employing plants as corrosion inhibitors is a physical direction to detect less expensive green friendly inhibitors. Researchers found that the "*Citrus aurantium* leaves extracts are mixtures containing vitamins, minerals, phenolic compounds and terpenoids. The flavonoids contained in *C. aurantium* can be divided into four groups, including flavones, flavanones, flavonols, and anthocyanins." These compounds indicate the extracts of *Citrus aurantium* leaves are appropriate to be applied as green corrosion inhibitors. Extracts of *Citrus aurantium* leaves have been researched by utilizing EIS, gravimetric and SEM techniques as novel eco-friendly corrosion inhibitors for carbon steel in corrosive environments. Inhibition effectiveness of tested extract depends on different concentrations of extract, starting from 0 to 40% v/v. Inhibition effectiveness of 81.2% is reached at the concentration of 20% v/v of the extract in 1 M corrosive solution for three hours at 25°C. Temperature effects and activation parameters have been investigated. A theoretical investigation of *Citrus aurantium* leaves extract isomers as corrosion inhibitors have been done using DFT/ B3LYP "density functional theory." The results shows that, in general, *Citrus aurantium* leaves have good inhibiting activities at relatively low concentrations. Phenolic groups of *Citrus aurantium* leaves were picked for examination as substituents of the four inhibitors. Hydroxyl groups of the studied extract compounds result in an increase in inhibition effectiveness, while methylation of the hydroxyl group leads to decrease in inhibitive effectiveness. *Citrus aurantium* leaves extracted isomers symbolize a considerable enhancement in the inhibition performance.

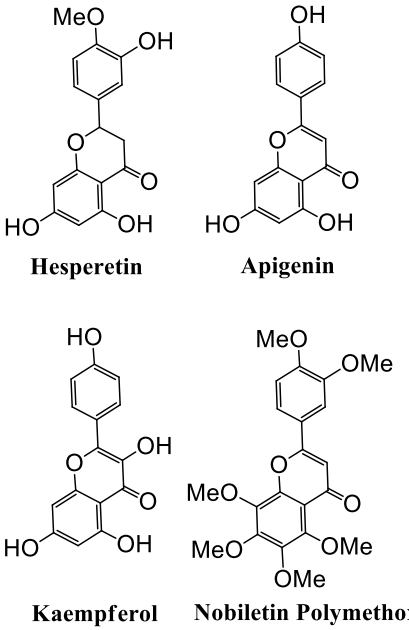
Keywords: *Citrus aurantium,* eco-friendly, corrosion, green inhibitor.

1. Introduction

The ecological effects of corrosion on alloys are huge, and the universal stature of the issue was encouraging researches s in this field. Corrosion is a considerable issue that should be faced for these reasons, first, safety, second environmental and third economical. Acids such as hydrochloric and/or sulfuric, acid mandate the employment of inhibitors molecules for the corrosion inhibition of alloys [1]. The object has a weak corrosive impedance, chiefly in corrosive solutions [2]. Inhibitors are natural or synthesized compounds that have the tendency to inhibit or impedate the corrosion rate [3]. Although there is a considerable number of inhibitors which were studied and used in the manufacturing process as corrosion inhibitors [4], but that are non or low toxicity, are now far more strategically than in the last decays. Research articles in the fields of corrosion inhibitors are directed towards the goal of developing and manufacturing low cost, efficient inhibitors at zero and low environmental effects [5]. Plants extracts are eco-friendly and cheap, and thus, the major feature of utilizing these extracts as inhibitors are because of economical and

*Corresponding author E-mail: taysersumer@atu.edu.iq

ecological interests. Nowadays, a significant number of plants extracts is utilized as efficient corrosive inhibitors of alloys in corrosive environments [6]. Although a number of organic molecules were synthesized as corrosion inhibitions, there is a requirement to promote inexpensive green inhibitors. A considerable number of plants extracts were examined as corrosion inhibitors for carbon steel [7-9] ". The impacts of chemical structure of the molecules on chemical reactivity were investigated extensively [10]. Recently, DFT "Density Functional Theory" has been effectively employed to realize the significance of chemical structure of un inhibitor and the adsorption performance on alloys [11]. Novel, exceedingly efficient inhibitors and various quantum chemical investigations were done that relate inhibition performance to geometrical characteristics of the various kind of molecules. The chemical structure in addition to electronic parameters, that may be acquired from theoretical estimations which are include the EHOMO "highest occupied molecular orbital energy" the ELUMO "lowest unoccupied molecular orbital energy," and the energy of the gap, impact the effectiveness of an inhibitor in addition to reactivity that may be treated by HSAB theory [12]. Continuing the previous studies on natural and synthetic organic inhibitors [13], the current investigation focuses on the impact of leaves extract of Citrus aurantium, as a corrosion inhibitor for CS "carbon steel," in HCl environment. The protection impact and the mechanism of corrosion were also investigated by mean electrochemical measurement (EIS) and gravimetric and SEM techniques. The electron configuration of *Citrus aurantium* leaves is isomerized, as in Scheme 1, using DFT elucidated, and we can also find out the relation of inhibitive performance and the structure of the extracts molecules.



Scheme 1. Structures of flavanones, flavonols, flavones, polymethoxyflavones found in *Citrus aurantium* leaves

2. Experimental Section

2.1 Materials (Preparation of Specimens).

The Carbon steel has been acquired and cut mechanically into small specimens, as described in reference [12].

2.2 EIS

Electrochemical impedance spectroscopy has been achieved as described in reference [13].

2.3 Plant extract

Fresh Citrus aurantium leaves were employed in this investigation. The plant was washed with distilled water many times and put on a tissue to dry. Citrus aurantium leaves of two grams were immersed for 48 h. in 100 ml of ethyl alcohol and then filtered.

2.4 DFT investigations

To evaluate the geometry of ground state, "Gaussian 03, Revision C.01 [14] has been optimized to a local minimum without symmetry restrictions, using the valence and polarization basis set (6-31G++(d,p)) [15, 16]. A combination of the Becke three-parameter hybrid (B3) exchange functional and the Lee-Yang-Parr (LYP) correlation functional (B3LYP) [17] and a version of the (DFT) method have been used to determine all optimized geometries", HOMO, LUMO and physical characteristics of the studied chemical compounds in this research. The obtained frontier molecular orbital energies, including EHOMO and ELUMO, help evaluate other considerable factors, ΔE, η, σ, χ, and ΔN utilizing [18,19] and the equations (1-5).

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (1)$$

$$\eta = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (2)$$

$$\sigma = \frac{1}{\eta} \quad (3)$$

$$\chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (4)$$

$$\Delta N = -\frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (5)$$

Where χ_{Fe} = *electronegativity,* η_{inh} = *hardness of Fe.*
The researchers published the χ_{Fe}, as equal to 7 eV/mol and η_{Fe} as equal to zero eV/mol [20]. Nowadays, researchers publish that the value of χ_{Fe} being equal to 7 eV is not reasonable because of electron/electron interactions, so ϕ (work function) of tested CS is employed instead of χ_{Fe}, as in equation (6)

$$\Delta N = -\frac{\varphi - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (6)$$

2.5 Characterization of surface

To study the surface modifications on the CS morphology before and after the addition of Citrus aurantium leaves extract, SEM "scanning electron microscopic" investigations are done. The CS coupons were, firstly, immersed without and with the Citrus aurantium leaves extract for 5 h at 303 K. After the exposure, the CS coupons were picked out, washed with water then alcohol, and dried, in order to analyze the morphology of the coupons.

3. Results and Discussion

3.1 Concentration of plant extract

CR "Corrosion Rate" of CS in one molar of corrosive solution with various extract contents was estimated after three hours immersion at 303 K. CRs and IEs "Corrosion Rate and Inhibition Efficiencies" are showed in Table 1. From Figs. 1 and 2, it can be seen that IE is raised with the increase of the extract concentration and reaches the highest value "80.2 at 20%" of the inhibitor, but CR decreases with the increase of the extract content. This action could be attributed to the adsorption of the inhibitor molecules that utilized this investigation on CS surface [21, 22].

Table 1. Corrosion rate, inhibition efficiency and weight loss "WL" for the tested plant extract

Extract content (%)	CR	IE%	WL
0	83.48×10^{-2}	----	27.9
5	24.91×10^{-2}	70.1507	7.61
10	22.89×10^{-2}	73.4285	7.13
15	19.30×10^{-2}	77.5913	6.74
20	17.05×10^{-2}	80.2070	5.92

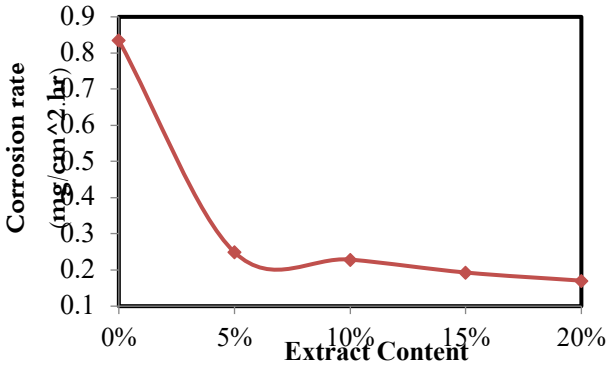


Figure 1. Corrosion rate of carbon steel with and without the extract in corrosive solution at 303K

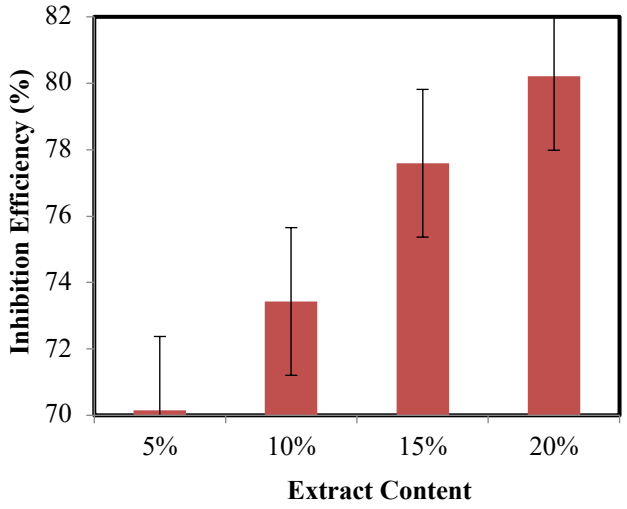


Figure 2. IE with the content of the extract in hydrochloric acid at 303 K

3.2 Temperature degrees

The temperature degrees impact on the WL "Weight Loss", C_R and IE were investigated in hydrochloric acid for three hours at temperatures (303, 313 and 323 K). As in Table 2 and Figs. 3 and 4, specified that the corrosion rate of carbon steel in absence and presence of the extract increases with raising the temperature degree, although CR is decreased in the solution that has the extracts compared with blank media, while inhibition efficiency increases with temperature degree increase. These results demonstrate that the adsorption of the tested extract on the carbon steel in HCl is chemi-sorption [23, 24].

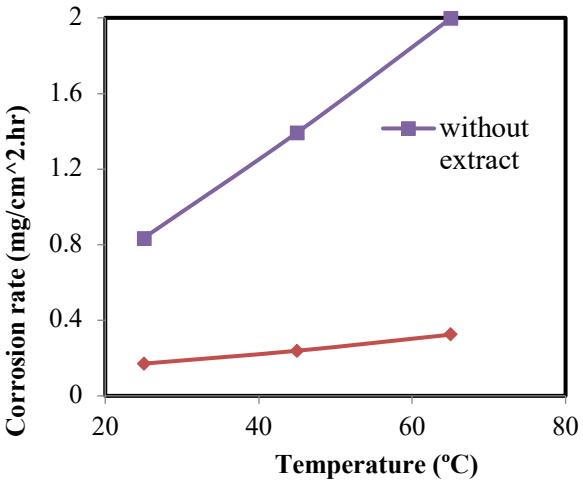


Figure 3. Corrosion rate of carbon steel of the extract in HCl at different temp. degrees

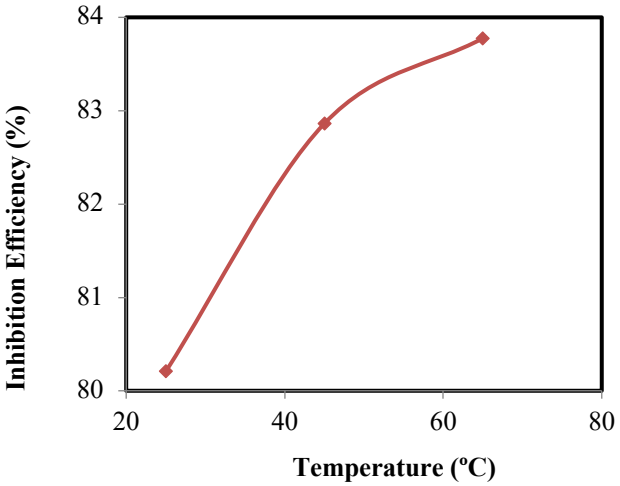


Figure 4. Inhibition efficiency of the extract in HCl at different temp. degrees

3.3 EIS

The methodological results which were achieved from EIS techniques for the corrosion of CS in the presence and absence of the *Citrus aurantium* leaves extract at 303 K are summarized in Table 2.

Table 2. CPE data for CS in corrosive environmet with various concentrations plant extract at 303K

Rs (ohm cm^2)	Rct (ohm cm^2)	CPE		Cdl (μFcm^{-2})	IE (%)
		Y_o (μS $s\alpha$ cm^{-2})	α		
0.2724	0.0869	9195	0.9228	339.1	0.00
0.3543	0.7688	3793	0.7036	822.6	51.63
0.3689	0.7728	1996	0.7734	956.2	73.94
0.3902	0.7974	1694	0.8132	366.1	80.26
0.5606	0.8572	433	0.8611	265.4	91.83

The impedance spectra for the CS coupons in 1.0 M corrosive media without and with various concentrations of *Citrus aurantium* leaves extract at 303 K are demonstrated as Nyquist plots in Fig. 5, and a considerable increase in the total impedance is observed with the addition of a corrosion inhibitor. In Figure 5, the impedance response of CS is considerably varied after the addition of the plant extract to HCl media. These results could be imputed to increase the substrate impedance and the plant extract concentrations. The analyzed results of EIS utilizes equivalent circuit [25], as displayed in Figure 6. IEs % have been calculated according to Eq. 7:

$$IE\% = \frac{R_{inh} - R_{uninh}}{R_{inh}} \qquad 7$$

Where R^o_{ct} *is the charge transfer resistance in the presence of Citrus aurantium* leaves extract, *and* R_{ct} *is the charge transfer resistances in the absence of Citrus aurantium* leaves extract.

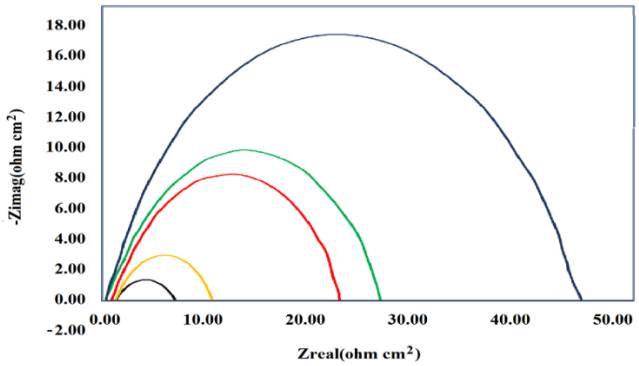


Figure 5. *Nyquist plots for CS in 1.0 M hydrochloric acid environment with different concentrations of Citrus aurantium* leaves extract *at 303K*

Through utilizing Gamry Software, EIS methodological information have been analyzed, which are data matching constant phase element (CPE) for CS coupons calculation solution impedance R and CPE, calculation of R_{ct}, and Cdl [26]. Table 2 demonstrates the EIS information for 1.0 M HCl with various plant extract concentrations at 303K, where the value of Cdl decreases and the value of Rct increases with the addition of plant extract. This is because of the gradual substitutions of water molecules by the adsorption of the plant extract molecules on the CS surface, and diminishing the extent of degradation reaction. The high values of Rct are usually related with slower corrosive systems [27, 28]. However, the decrease of the value of Cdl results from the electrical double layer thicknes increase [29]. This confirms that the plant extract molecules are absorbed on the CS surface and form a protective layer. Big impedance transfer charges proportional with systems that corrode slowly [30]. With the Rct value increase, the IE also increases; it reached to 91 % at the highest utilized concentration.

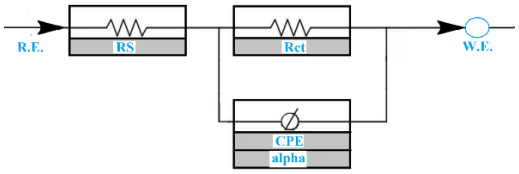


Figure 6. *Equivalent model, utilized to fit resistance information for CS in the corrosive solution in the absence and presence of Citrus aurantium* leaves extract

3.4 SEM

The morphology of the surface of CS coupons in an acidic environment without and in addition of *Citrus aurantium* leaves extract, exposed for five hours at 303 K, have been done through SEM "scanning electron microscopy". The carbon steel coupons exposed to one molar of hydrochloric acid are undergoes significant corrosion demonstration in Fig. 7a. Furthermore, a smooth surface with low damage is spotted in the case of the carbon steel with more Citrus *aurantium* leaves extract (Figure 7b), which indicates that CS is protected from the corrosive solution by the addition of *Citrus aurantium* leaves extract.

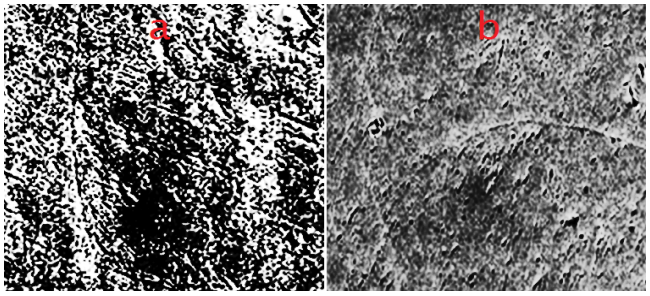


Figure 7. SEM images

3.5 Computational calculations

Four different compounds have been picked as the types of molecules, namely, Hesperetin, Apigenin, Kaempferol and Nobiletin to include the most significant electronic impacts. The four compounds are a strong donor. The positions of the hydroxy and methoxy groups substituent on the benzene and pyran rings in the selected compounds were "C-1, C-2, C-3, C-6, C-8, C-12 C-13, C-14, C-15 and C-16". These positions make the same contribution to both the HUMO and LUMO levels with a small difference, as shown in Fig. 8. Fig. 8 also demonstrates the structures of the optimized geometries for Hesperetin, Apigenin, Kaempferol and Nobiletin. Table 3 demonstrates the energies of the "HOMO, LUMO and energy gap" values for Hesperetin, Apigenin, Kaempferol, Nobiletin and all models. I "ionization potential" and "electron affinity" have been estimated through employment of Koopman's theorem [31]. This theorem confirms a correlation between the HOMO and LUMO energies in addition to I and A, respectively.

Table 3. Q-CP "Quantum-chemical parameters" for Hesperetin, Apigenin, Kaempferol and Nobiletin, as showed by DFT

Comp.	HOMO (eV)	LUMO (eV)	ΔE (eV)	(I)	(A)
Hesperetin	-10.84	-3.65	7.18	10.83	3.65
Apigenin	-11.62	-4.37	7.24	11.62	4.37
Kaempferol	-10.40	-3.59	6.43	10.40	3.59
Nobiletin	- 9.28	-4.31	4.97	9.285	4.31

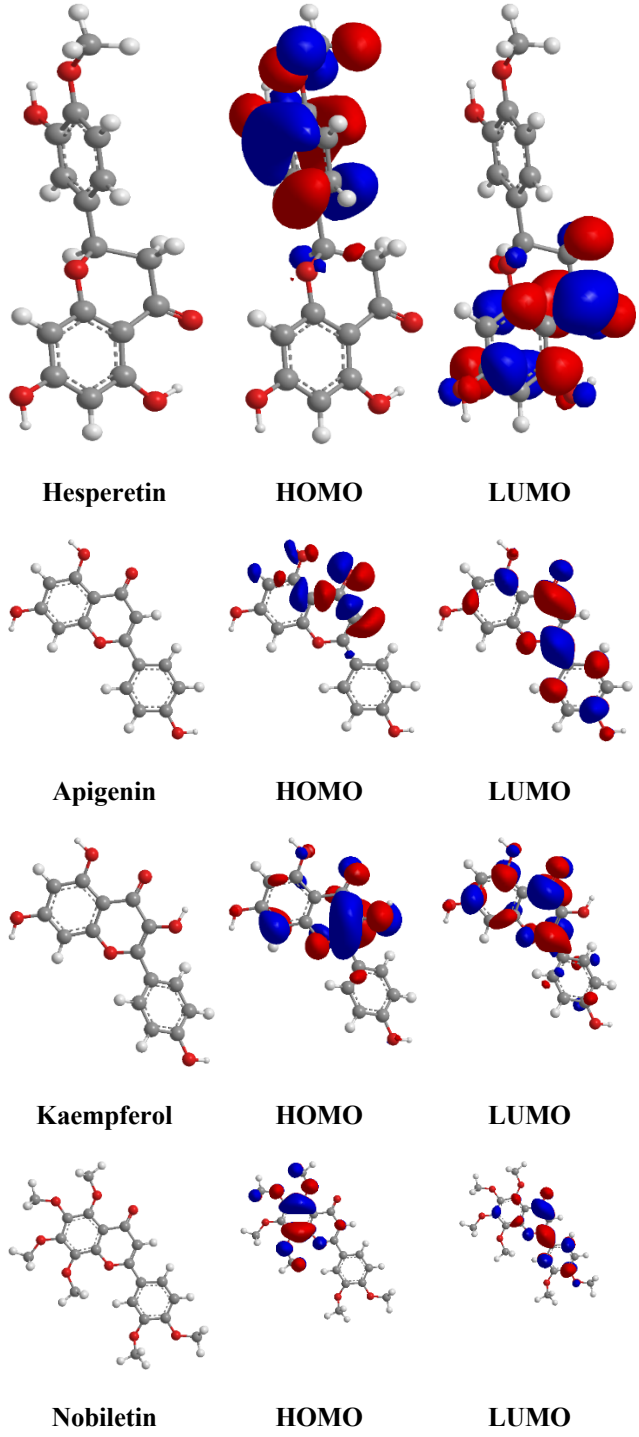


Figure 8. The optimized structures for Hesperetin, Apigenin, Kaempferol and Nobiletin

I = - EHOMO

A = - ELUMO

Table 4 shows the values that calculated the IE % for Hesperetin, Apigenin, Kaempferol and Nobiletin that were determined utilizing the following formula:

$$Iadd.\% = IMol - I \times 100\ \%$$

$$Ieadd.\% = Iadd.\% \times IeMI\ \%$$

$$Ietheor.\% = IeMI\% + Ieadd.\%$$

"Where $I_{add.}$% is the percentage of ionization potential of the additive for compounds (x - MI), $Ie_{add.}$% is the inhibition efficiency % of the additive, and $Ie_{theor.}$% is the theoretically calculated percentage inhibition efficiency."

Table 4. The calculated IE % of Hesperetin, Apigenin, Kaempferol and Nobiletin

Molecules	**% $I_{add.}$**	**% $Ie_{add.}$**	**IE %, theoretical ($Ie_{theor.}$)**
Hesperetin	+17.112	+13.273	88.936
Apigenin	+16.488	+12.178	87.442
Kaempferol	+8.782	+5.328	77.216
Nobiletin	-11.243	-8.662	44.623

Results showed that methoxide groups of green inhibitors progress to a diminution in inhibition effectiveness. The maximum effective inhibitors were Apigenin and Hesperetin, which displayed an inhibition efficiency of 88.9 % and 87.4 % respectively. In contrast, hydroxyl group lead up to an increase in IE, but on other hand, the steric handers decrease the inhibition activity as in Nobiletin, which displayed an inhibition efficiency of 44.623%. DFT data are especially helpful in getting more information on inhibitive phenomenon. Inhibitive performance of a plant extract is correlated with theoretical parameters such as HOMO, LUMO, ΔE, η, σ, χ and ΔN, as in Eq. 8. These factors can be seen by the optimization of the tested inhibitor molecule [32]. These factors give a glance at understanding the CS interaction with inhibitor molecules. In this investigation, all of the quantum parameters were calculated for Hesperetin molecules. These investigations were summarized in Table 5.

Table 5. DFT factors for Hesperetin

Parameters	Calculations
HOMO (eV)	-10.834
LUMO (eV)	-3.653
ΔE (eV)	7.181
Hardness (η)	3.5905
Softness (σ)	0.278
Electronegativity (χ)	7.243
fraction of electrons transferred (ΔN)	0.369
Dipole moment	3.992
Electron affinity (A)	10.834
Ionization potential (I)	3.653

In the geometrical optimization of Hesperetin, as displayed in Fig. 9, IE can be acknowledged by energies of HOMO and LUMO, for Hesperidin's factors are demonstrated in Fig 9.

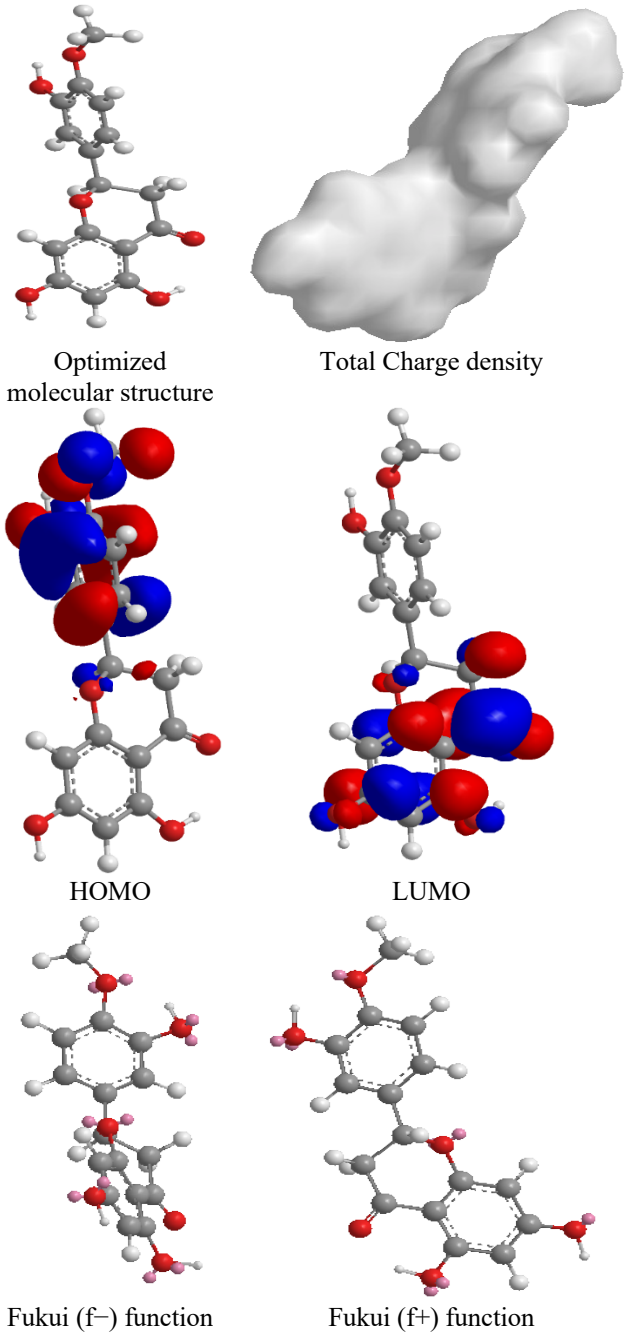


Figure 9. Optimization, total electron density, HOMO, LUMO and Fukui functions of Hesperetin

The HOMO value displays the ability of donation electrons of the inhibitor. HOMO with a high value indicates that the

tested molecules have high value affinity. LUMO illustrates the capability of accepting electrons. The low value of LUMO reveals that the inhibitor has the ability to accept free electrons from the metal surface via back-donation. The low value of ΔE recommends significance of IE of the tested inhibitor. IE increases with σ increase and decreases on η increase. η and σ are considerable parameters that provide data about reactivity and stability [33]. It can be concluded that η with a low value propose a higher IE. In Hesperetin molecules (Figure 9), Table 5 demonstrates that the ΔE value for Hesperetin (7.181eV) and the values of σ with η, and in addition to ΔN for Hesperetin are in good agreement with methodological results. The value of χ is 7.2435, that in good indication that Hesperetin molecules have excellent inhibition efficiency. ΔN provides data about the number of electrons in which a molecule transfers to the empty orbital [34].

Dipole moment (μ) is the polarity measurement of a covalent bond. It is the effect of charges on the bonded atoms and the distance. An inhibitor with a high value of dipole moment (μ) has ability to form potent interactions with the metal surface, which results in a potent adsorption on CS surface, leading to a good IE. Inhibition techniques may be demonstrated according to dipole moment. Hesperetin molecules have a dipole moment of 3.992, and IE is equal to 91.83%.

3.6 Mulliken charge

Mulliken Atomic charges are significant for assessing the adsorption centers of the investigated molecules. Charges with high values, demonstrate the capability of tested molecules to be adsorbed on CS surface. Oxygen and some carbon atoms in the Hesperetin molecules have high values of negative charges which refer to complexation reaction with iron atoms, as demonstrated in Table 6 and Fig. 10. Therefore, carbon and oxygen atoms are the active centers, which have the capability to be coordinated with CS surface. Hesperetin molecules could accept unpaired electrons from the surface of CS, due to positive charges carbon atoms that were often sites where nucleophiles could attach. Nowadays, some investigators publish that good inhibitors have the capability to donate and accept electrons with the metal [33-35].

Table 6. Mulliken charges of heteroatoms present in hesperetin

At.	CH.	At.	CH.	At.	CH.
C1	0.20	O10	-0.26	O19	-0.23
C2	-0.24	C11	-0.08	O20	-0.24
C3	0.27	C12	-0.03	O21	-0.30
C4	-0.34	C13	0.08	C22	0.21
C5	0.23	C14	0.06	H23	0.08
C6	-0.17	C15	-0.09	H24	0.09
C7	0.29	C16	-0.02	H25	0.04
C8	-0.06	O17	-0.33	H26	0.04
C(9	0.19	O18	-0.24	H27	0.00

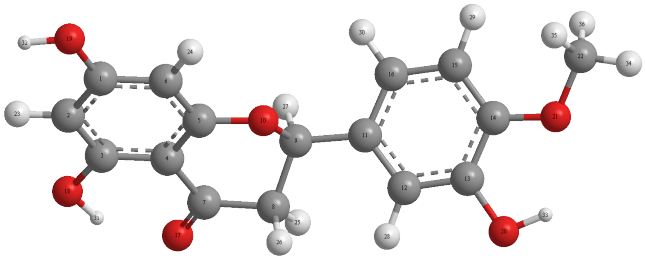


Figure 10. The optimized chemical structure of hesperetin molecule with atoms numbers

4. Conclusions

Citrus aurantium leaves extract have been selected as an efficient ecofriendly inhibitor on CS in one molar hydrochloric acid. The extract demonstrates excellent inhibition efficiency at the inhibitor concentration of 20% in v/v for three hours at 25°C. The inhibition efficiency has been increasing in parallel with the increasing temperature degree of solution. DFT calculations confirmed the relation between parameters "related to electronic structure" and the inhibition potential of the four tested compounds, Hesperetin, Apigenin, Kaempferol and Nobiletin. The structural parameters estimated at "B3LYP/6-311G++(d,p) level" specified that the steric hinders lead up to a decrease the IE, while hydroxyl groups lead up to increasing in IE.

Competing interests

The authors declare that they have no competing interests.

Acknowledgement

The authors thank UKM-YSD Chair on Sustainable Development for the Grant 020-2017 'Malaysia' for supporting this work

References

[1] A. Prithiba and R. Rajalakshmi. An ecofriendly Initiative for the Corrosion Inhibition of Mild Steel in 1 M HCl Using Tecoma capensis Flower Extract. *International Journal of Metals,* **2016**, 1-9, 2016.

[2] K. K. Alaneme, S. J. Olusegun, and O. T. Adelowo. Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel iersed in acidic solutions. *Alexandria Engineering Journal,* **55**, 673–681, 2016

[3] A. Praditya, S. Shahab, L. Noerochim, and D. Susanti, Inhibition of corrosion of carbon steel in 3.5% NaCl solution by Myrmecodia pendans extract. *International Journal of Corrosion*, **2016**, 1-6, 2016.

[4] A. Braihi A. Jawa A. Kadhum, H. Aljibori, A. Al-Amiery and L. Shaker. *Chemical resistance of NR/SBR rubber blends for surfaces corrosion protection of metallic tanks in petrochemical industries*. *Koroze a ochrana materiálu*, **64**, 65-71, 2020.

[5] S. Deng, X. Li. Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H_2SO_4 solutions. Corros. Sci., **55**, 407-415, 2012

[6] A. Al-Amiery and L. Shaker. Corrosion inhibition of mild steel using novel pyridine derivative in 1 M hydrochloric acid. *Koroze a ochrana materiálu*, **64**, 59-64, 2020.

[7] T.A. Salman, D.S. Zinad, S.H. Jaber, M. Al-Ghezi, A. Mahal, M.S. Takriff and A. Al-Amiery. Effect of 1,3,4-thiadiazole scafold on the corrosion inhibition of mild steel in acidic medium: an experimental and computational study. J. BioTribo-Corrosion, **5**, 1, 2019.

[8] H.J. Habeeb, H.M. Luaibi, R.M. Dakhil, A.A.H. Kadhum, A. Al-Amiery and T.S. Gaaz. Development of new corrosion inhibitor tested on mild steel supported by electrochemical study. *Results Phys.*, **8**, 1260, 2018.

[9] A. Al-Amiery, A. Kadhim, A. Mohamad, A. Musa, and C. Li, Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hydrochloric acid. *Materials*, **6**, 5466, 2013.

[10] S. Junaedi, A. Kadhim, A. Al-Amiery, A. Mohamad and M. Takriff. Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino5-Oleyl1,3,4-Thiadiazol (AOT). *Int. J. Electrochem Sci.*, **7**, 3543, 2012.

[11] A. Kadhim, A. Al-Okbi, D.M. Jamil, A. Qussay, A. Al-Amiery, T.S. Gaaz, A.A.H. Kadhum, A.B. Mohamad and M.H. Nassir. Experimental and theoretical studies of benzoxazines corrosion inhibitors. *Results Phys.* **7**, 4013, 2017.

[12] K.F., Al-Azawi, I.M. Mohammed, S.B. Al-Baghdadi, T.A. Salman, H.A. Issa, A. Al-Amiery, T.S. Gaaz, and A.A.H. Kadhum, Experimental and quantum chemical simulations on the corrosion inhibition of mild steel by 3-((5-(3,5-dinitrophenyl)-1,3,4- thiadiazol-2-yl)imino)indolin-2-one, *Results Phys.*, **9**, 278, 2018.

[13] A. Mohamad, A. Kadhum, A. Al-Amiery, L. Ying and A. Musa. Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0 M H_2SO_4. *Met. Mater. Int.*, 20, 459, 2014.

[14] S.B. Al-Baghdadi, F.G. Hashim, A.Q. Salam, T.K. Abed, T.S. Gaaz, A. Al-Amiery, A.A.H. Kadhum, K.S. Reda and W.K. Ahmed, Synthesis and corrosion inhibition application of NATN on mild steel surface in acidic media complemented with DFT studies. *Results Phys*., **8**, 1178, 2018.

[15] A.H.M.J. Al-Obaidy, A. Kadhum, S.B. Al-Baghdadi, A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad and E. Yousif. Eco-friendly corrosion inhibitor: experimental studies on the corrosion inhibition performance of creatinine for mild steel in HCl complemented with quantum chemical calculations. *Int. J. Electrochem Sci*., **10**, 3961, 2015.

[16] A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad and S. Junaedi. A Novel hydrazinecarbothioamide as a potential corrosion inhibitor for mild steel in HCl. *Materials*, 6, 1420, 2013.

[17] M.H.O. Ahmed, A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum, A.B. Mohamad and T.S. Gaaz, Synthesis and characterization of a novel organic corrosion inhibitor for mild steel in 1 M hydrochloric acid, *Results Phys*., **8**, 728, 2018.

[18] T. A. Salman, A. Al-Amiery, L. M. Shaker, A. Kadhum and M. S. Takriff, A study on the inhibition of mild steel corrosion in hydrochloric acid environment by 4-methyl-2-(pyridin-3-yl)thiazole-5-carbohydrazide. *Int. J. Corros. Scale Inhib*., **8**, 1035, 2019.

[19] T. A. Salman, Q.A. Jawad, M. A. Hussain, A. Al-Amiery, L. M. Shaker, A. Kadhum and M. S. Takriff. Novel ecofriendly corrosion inhibition of mild steel in strong acid environment: adsorption studies and thermal effects. *Int. J. Corros. Scale Inhib*., **8**, 1123, 2019.

[20] S.S. Al-Taweel, K.W.S. Al-Janabi, H.M. Luaibi, A. Al-Amiery and T.S. Gaaz. Evaluation and characterization of the symbiotic effect of benzylidene derivative with titanium dioxide nanoparticles on the inhibition of the chemical corrosion of mild steel. *Int. J. Corros. Scale Inhib.* **8**, 1149, 2019.

[21] D.S. Zinad, Q.A. Jawad, M.A.M. Hussain, A. Mahal, L. M. Shaker and A. Al-Amiery. Adsorption, temperature and corrosion inhibition studies of a coumarin derivatives corrosion inhibitor for mild steel in acidic medium: gravimetric and theoretical investigations. *Int. J. Corros. Scale Inhib.*, **9**, 134, 2020.

[22] S. Tu, X. H. Jiang, L. M. Zhou, M. Duan, H. Wang, X. M. Jiang. Synthesis of N-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides and their corrosion inhibition activities on X70 steel in 5 M HCl. *Corros. Sci.*, **65**, 13−25, 2012.

[23] M. A. Hegazy, A. M. Hasan, M. M. Emara, M. F. Bakr and A. H. Youssef. Evaluating four synthesized Schiff bases as corrosion inhibitors on the carbon steel in 1 M hydrochloric acid. *Corros. Sci.*, **65**, 67−76, 2012.

[24] L. R. Chauhan, G. Gunasekaran. Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corros. Sci*., **49**, 1143−1161, 2007.

[25] A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum and A.B. Mohamad. New coumarin derivative as an eco-friendly inhibitor of corrosion of mild steel in acid medium. *Molecules*, **20**, 366, 2015.

[26] A.Y.I. Rubaye, A.A. Abdulwahid, S.B. Al-Baghdadi, A. Al-Amiery, A.A.H. Kadhum and A.B. Mohamad. Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/MS spectroscopy. *Int. J. Electrochem Sci.*, **10**, 8200, 2015.

[27] A. Kadhum, A. Mohamad, A.A.H. Kadhum, A.B. Mohamad, L.A. Hammed, A. Al-Amiery, N.H. San and A.Y. Musa. Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. *Materials*, **7**, 4335, 2014.

[28] D.S. Zinad, M. Hanoon, R.D. Salim, S.I. Ibrahim, A. Al-Amiery, M.S. Takriff and A.A.H. Kadhum. A new synthesized coumarin-derived Schiff base as a corrosion inhibitor of mild steel surface in HCl medium: gravimetric and DFT studies. *Int. J. Corros. Scale Inhib*., **9**, 228, 2020.

[29] Q. A. Jawad, D. S. Zinad, R. D. Salim, A. Al-Amiery, T. S. Gaaz, M. S. Takriff and A. Kadhum. Synthesis, characterization, and corrosion inhibition potential of novel thiosemicarbazone on mild steel in sulfuric acid environment. *Coatings*, **9**, 729, 2019.

[30] A. Al-Amiery. Antimicrobial and antioxidant activities of new metal complexes derived from (E)-3-((5-phenyl-1,3,4-oxadiazol-2-ylimino) methyl)naphthalen-2-ol. *Med. Chem. Res.*, **21,** 3204, 2012.

[31] D.M. Jamil, A.K. Al-Okbi, S.B. Al-Baghdadi, A. Al-Amiery, A. Kadhim and T.S. Gaaz. Experimental and theoretical studies of Schiff bases as corrosion inhibitors. *Chem. Cent. J.*, **12**, 1, 2018.

[32] E. Yousif, Y. Win, A. Al-Hamadani, A. Al-Amiery, A. Kadhum and A. Mohamad, Furosemi as an environmental-

friendly inhibitor of corrosion of zinc metal in acid medium experimental and theoretical studies. *Int. J. Electrochem Sci.* **10**, 1708, 2015.

[33] J.A.A. Yamin, E. Ali Eh Sheet and A. Al-Amiery. Statistical analysis and optimization of the corrosion inhibition efficiency of a locally made corrosion inhibitor under different operating variables using RSM. *Int. J. Corros. Scale Inhib*., **9**, 502, 2020.

[34] R.D. Salim, Q.A. Jawad, K.S. Ridah, L.M. Shaker, A. Al-Amiery, A.A.H. Kadhum and M.S. Takriff. Corrosion inhibition of thiadiazole derivative for mild steel in hydrochloric acid solution, *Int. J. Corros. Scale Inhib.* **9**, 550, 2020.

[35] A. Al-Amiery, L.M. Shaker, A.A.H. Kadhum, M.S. Takriff, Corrosion Inhibition of Mild Steel in Strong Acid Environment by 4-((5,5-dimethyl-3-oxocyclohex-1-en-1-yl)amino)benzenesulfonamide. *Tribology in industry,* **42**, 89, 2020.