Corrosion Inhibition Potential of *Mentha spicata* Extract on Mild Steel in Acidic Medium

Bhawsar, Jeetendra**•; Jain, Pramod

Department of Chemistry, Government Holkar (Model, Autonomous) Science College, Indore, (M.P.) INDIA

ABSTRACT: The corrosion inhibition effect of Mentha spicata extract has been investigated for mild steel in an acidic medium by using weight loss and thermometric methods. Qualitative and Quantitative analysis of the extract was carried out using GC/MS analysis. Two major phytochemical components were identified by their mass spectra and retention indices. The inhibition capacity of Mentha spicata extract observed were carried at different temperatures (303 K, 313 K, 323K, and 333 K) which were found to increase with increasing concentration but decrease with increasing temperature. As the extract components got adsorbed on the metal surface, inhibition efficiency also increased and finally reached 86.01% at 303 K. The adsorption isotherm and free energy values were also calculated. Results have demonstrated that Mentha spicata is a mixed-type of corrosion inhibitor. Surface analysis by SEM documented the formation of a protective layer on the mild steel surface. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), and Total Energy (TE) were calculated. Quantum chemical calculations were also discussed to support the experimental data and the adsorption of inhibitor molecules onto the metal surface. It has been found that the extract acts as an effective corrosion inhibitor for mild steel in a hydrochloric acid medium. The results obtained show that Mentha spicata extract could serve as an excellent eco-friendly green corrosion inhibitor.

KEYWORDS: *Plant Extract; Mass loss; Free energy; Regression; Density Functional Theory; Surface Morphology.*

INTRODUCTION

Metals have industrial significance on account of being economical and high strength mild steel is mostly used in making tanks, petroleum refinery equipment, pipes, boilers, etc. [1,2]. Acid solutions are used for cleaning scales and unwanted rust in industrial processes [3]. Generally, Hydrochloric acid and Sulphuric acid are used in the descaling process which leads to the dissolution of the metal. HCl is most widely used for the acidizing procedure [4] and that is why the main focus is on this acid. To protect the metal surface from corrosive environments many techniques have been used such as selection of material, design change, coatings, anodic /cathodic protection, and corrosion inhibitors. Which corrosion inhibitors are the best option for corrosion mitigation of metal [5]. Various organic and inorganic chemical compounds have been used as corrosion inhibitors but these are expensive and toxic to the environment and human health [6-10]. Due to the environmental consequences of developing eco-friendly

^{*} To whom correspondence should be addressed.

⁺ E-mail: jitendra.bhawsar@gmail.com

[•] Other Address: Department of Chemistry, Medi-Caps University, Pigdamber, Rau, Indore, (M.P.), 453331, INDIA 1021-9986/2022/10/3365-3376 12/\$/6.02

corrosion inhibitors is much more favorable [11-13]. In the last decade, scientists have been working on green corrosion inhibitors. Extracts of plant leaves, seeds, bark, stem, and fruits are highly preferred because these are cheap, readily available, eco-friendly, and renewable sources of materials. Some of the plant extracts have been found effective corrosion inhibitors in HCl medium also [14-16].

Recently Wang et al. [17] reported that Solanum lasiocarpum extract gives adequate protection 93.31% at a concentration of 1 g/L to steel in 1M HCl solution. Belarbi et al. [18] studied Algerian L. stoechas oil as a corrosion inhibitor for carbon steel in 1M hydrochloric acid, by estimating the impact of essential oil and found that the oil mitigate the corrosion of metal upto 61.97%. Fouda et al. [19] found that Punica plant extract can be a good inhibitor for C steel in HCl solutions. Dhaundiyal et al. [20] investigated the effect of Origanum vulgare extract as a corrosion inhibitor for mild steel in HCl solution using the weight loss method. Results showed that the inhibition efficiency of the inhibitor increased with the elevation of extract concentration. [17-20] Mentha spicata is a perennial herb; a member of the Labiatae family. This family contains polyphenolic compounds and its leaf extracts possess great antioxidant properties [21]. Thus, due to the strong antioxidants present in Mentha spicata, the leaf extracts are used to control the corrosion of mild steel in a 2M HCl medium. The major phytochemicals present in the extract contain heteroatoms (S, N, O, P) which can be adsorbed on metal surfaces and provide a protective layer for corrosion inhibition. This natural plant material can substitute artificial corrosion inhibitors. The objective of this work is to investigate the corrosion inhibitory activity of leaf extract of Menta spicata on mild steel surface in an acidic medium using weight loss and thermometric methods at different temperatures. Furthermore, Quantum chemical-based theoretical investigations were carried out to explain the reactivity and adsorption characteristics of green inhibitor.

EXPERIMENTAL SECTION

Preparation of Leaves Extract

In the present study ethanolic extracts were derived from *Mentha spicata* plant. The washed plant material was dried in shade and grinded to powder form. 50g powder was weighed and refluxed with one liter of methanol [22]. The extract of *Mentha spicata* leaves obtained in this manner was used as a corrosion inhibitor.

Preparation of test solution

The aggressive solution (2M HCl) was prepared by dilution of Analytical Grade 98% HCl with doubledistilled water. The solution volume was 100 mL with and without the addition of different concentrations of *Mentha spicata* extract ranging from 1 g/L to 6 g/L.

Specimen preparation

The mild steel specimens with dimensions $(4 \times 2 \times 0.1 \text{ cm})$ were polished to a mirror finished with emery paper and degreased with acetone.

Characterization of Mentha spicata extracts (GC/MS Analysis)

The GC-MS analysis of *Mentha spicata* leaves extract was performed using Shimadzu QP-2010 plus with thermal desorption system TD 20 and a gas chromatograph interfaced with a mass spectrometer.

Gravimetric measurement (Weight loss method)

In the weight loss experiments, the difference between the initial and final weight of specimens taking place throughout exposure being expressed as corrosion rate [23]. The performed test was preferred by ASTM [24]. In this measurement rectangular mild steel samples completely immersed in 100 ml of the test solution in the presence and absence of the inhibitor at different temperatures (303K, 313K and 323K) for 6 hours. After the elapsed time, weight loss was taken as the difference in weight of the specimens. The reproducibility of the experiment was assured by running the tests in triplicate. The values of Corrosion rates, inhibition efficiency, and surface coverage were calculated from the following equations:

Corrosion Rate (mmpy) =
$$\frac{87.6 \times W}{DAT}$$
 (1)

Where, mmpy = illimeter per year, W = Weight loss (mg), D = Density (gm/cm³), A = Area of specimen (cm²), T = time in hours.

The inhibition efficiency (% *IE*) and degree of surface coverage (θ) were calculated using Equation (2) and Equation (3), respectively.

(Peak#	R. Time	Area%	Molecular formula	Molecular weight	Name
	1	28.836	12.20	$C_{14}H_{22}O_2$	222	3-Penten-2-one,4-(2,2,6-Trimethyl-7-Oxabicyclo[4.1.0]hept- 1-YL)-, (E)- (PC1)
	2	42.643	18.99	C ₂₉ H ₄₈ O	412	Stigmast-4-EN-3-one

Table 1: Chemical constituents present in the methanolic extract of Mentha spicata.

% IE =
$$\frac{(W1 - W2)}{W1} \times 100$$
 (2)

$$\theta = \frac{(W1 - W2)}{W1} \tag{3}$$

Where W_1 and W_2 are the weight loss without and with respectively.

Thermometric method

Inhibition efficiency was calculated by the thermometric method which was carried out according to the method described by *Eddy et al.* [25]. From the rise in temperature per minute, the reaction number (*RN*) and inhibition efficiency (%*IE*) were calculated using equations 4 and 5.

$$RN(^{\circ}C/\min) = \frac{T_{m} - T_{i}}{t}$$
(4)

where T_m is the maximum temperature attained by the system, Ti is the initial temperature and t is the time. From the above, the inhibition efficiency (%IE) of the used inhibitor will be computed by using the equation given below

$$\% IE = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100$$
(5)

Where RN_{aq} is the reaction number of aqueous acid in the absence of inhibitor, and RN_{wi} is the reaction number of aqueous acid in the presence of inhibitors.

Quantum chemical study

The metal surface and inhibitor interaction can be better understood by the computational chemistry method [26]. Density Functional Theory is the most powerful tool to explore the molecular structure and electronic parameters of inhibitor molecules. This method is very fast and provides some vital parameters with high accuracy [27,28]. The structures of major phytochemical molecules were fully and geometrically optimized using Density



Fig. 1: GC/MS chromatogram of Mentha spicata plant extract.

Function Theory (DFT) with the functional hybrid B3LYP (Becke, three-parameter, Lee-Yang-Parr exchangecorrelation function) DFT formalism with electron basis set 6-31G (d,p) using the Gaussian 09 for windows [29]. The quantum chemical parameters such as E_{HOMO} , E_{LUMO} , energy difference (ΔE), dipole moment (μ), and total energy were calculated [30].

RESULTS AND DISCUSSION

Identification of phytocomponents

The phytochemical components of the methanol extract of *Mentha spicata* plants have been analyzed by the GC/MS analysis. The GC/MS analysis of *Mentha spicata* revealed the presence of 48 compounds identified in the methanolic extract (Fig. 1). The active principles with their molecular formula, retention time, molecular weight and peak area ascertained (Table 1). On comparison of the mass spectra of the constituents with the NIST library, the two prominent peaks with retention time as 3-Penten-2-one,4-(2,2,6-Trimethyl-7-Oxabicyclo[4.1.0]hept-1-YL)-, (E)- (28.836) and Stigmast-4-en-3-one (42.643) were identified (Fig. 2). The active phytochemical constituents could possess corrosion inhibiting efficiency [22,31].



Fig. 2: Molecular Structure of major phytochemical constituents present in Mentha spicata plant extract

Gravimetric measurement

The influence of the concentration of Mentha spicata extract tested on the mild steel corrosion in 2M Hydrochloric acid solution was studied by weight loss measurements at 303K, 313K, 323K, and 333K after 6 hours of immersion period. The results obtained in the absence and presence of the different concentration of Mentha spicata extract is shown in Figs. 3-4 and corresponding data are listed in Table 2. It can be observed that the corrosion rate decreases and inhibition efficiency increases with increasing inhibitor concentration which shows the adsorption of molecules on the mild steel surface [32]. The highest inhibition efficiency value was obtained at a concentration of 6g/L 86.01% at 303K temperature. This behavior can be attributed to the adsorption and surface coverage of phytochemical components of the Mentha spicata extract onto the metal surface resulting in the blocking of the reaction sites and retard corrosion.

Effect of temperature

The weight loss experiments were performed at different temperatures from 303K-333K. Thermodynamic parameters were used to study the effect of temperature which is most important to have an idea about the stability

of the inhibitor film on metal surface. The results showed that the inhibition efficiency decreases with an increase in temperature. In acidic media, the evolution of hydrogen gas usually accelerates the corrosion reactions resulting in a higher rate of corrosion [33].

Adsorption isotherm

To determine the interaction between the inhibitor molecule and the metal surface, the adsorption of the extract on the surface was studied by adsorption isotherm. The adsorption isotherms explain the mechanism of corrosion inhibition by preparing a protective layer, due to the formation of either electrostatic or covalent bonding between the adsorbents and the metal surface atoms [25]. Langmuir adsorption isotherm exhibited the best fit for the adsorption of inhibitor molecules on mild steel surfaces [34]. This isotherm can be expressed by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{6}$$

C is the inhibitor concentration, θ is the fraction of the surface covered, K_{ads} is the adsorption coefficient. In Fig. 5, the plots of C/ θ versus C were fitted with straight line

	spicata entraci fi e	in a cigitt to	ss measur	ententisjor	o n ar argjer	ent tempere			
Immersion	Concentration of inhibitor	303 K		313K		323K		333K	
Period	(g/L)	CR (mmpy)	(%) IE	CR (mmpy)	(%) IE	CR (mmpy)	(%) IE	CR (mmpy)	(%) IE
	BLANK	56.49	-	411.26	-	288.98	-	451.25	-
	1	20.92	62.9	184.13	55.23	157.16	45.62	250.39	44.51
	2	18.83	66.6	141.58	65.57	141.35	51.09	238.06	47.24
6 h	3	12.78	77.37	119.73	70.89	114.61	60.34	181.57	59.76
	4	11.39	79.83	102.29	75.13	96.71	66.53	169.95	62.34
	5	9.99	82.31	83.46	79.71	77.42	73.21	151.58	66.41
	6	7.9	86.01	72.77	82.31	67.89	76.51	126.01	72.08

 Table 2: Corrosion parameters for mild steel in 2M HCl solution in absence and presence of different concentrations of Mentha

 spicata extract from weight loss measurements for 6 h at different temperature



Fig. 3: Concentration of inhibitor (g/L) and Corrosion Rate (mmpy) of mild steel in various concentrations of Mentha spicata extract at different temperatures in 2M HCl solution.

with regression coefficients are (0.995) at 303K, (0.996) at 313K, (0.980) at 323K, (0.977) at 333K, which is almost unity, confirming that the adsorption procedure obeyed Langmuir adsorption isotherm.

The free energies of adsorption, ΔG_{ads} , were calculated from the equilibrium constant of adsorption using the following equation:

$$\Delta G_{ads} = -2.303 \text{RT} \log [55.5 \text{Kads}] \tag{7}$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature.

Generally, it is observed that the values of ΔG_{ads} around -20 kJ/mol or lower are suggested [physisorption], which arises due to the electrostatic interaction between the



Fig. 4: Concentration of inhibitor (g/L) and Inhibition efficiency (%IE) of mild steel in various concentrations of Mentha spicata extract at different temperatures in 2M HCIsolution.

charged inhibitor molecules and the charged metal surface and around -40 kJ/mol or higher it suggests chemisorptions which involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate-type metallic bond [35].

The average value of K_{ads} was 0.994 L/g which was obtained from the reciprocal of the intercept of Langmuir plot line (Table 3). In the present study the values of ΔG_{ads} obtained were -11.04 kJ/mol at 303K, -10.88 kJ/mol at 313K, -9.72 kJ/mol at 323K and -10.07 kJ/mol at 333K, which indicates that the adsorption mechanism is physisorption, thus the corrosion inhibition occurs by the film formation of inhibitor molecules on metal surface [36,37]. The ΔG_{ads} values were negative, indicating the spontaneous adsorption of inhibitor molecules on the metal surface.

		<u> </u>	
Temperature (K)	K _{ads} (l/g)	Slope	$-\Delta G_{ads} (kJ/mol)$
303	1.440	1.065	11.04
313	1.179	1.090	10.88
323	0.671	1.086	9.72
333	0.684	1.190	10.07
Average	0.994	1.107	10.43

Table 3: Langmuir adsorption constant and change in free energy at different temperatures.

 Table 4: Reaction number (R.N.) and inhibition efficiencies (%IE) of various concentrations of methanol extract of Mentha

 spicata for mild steel in 2M HCl solution at 30°C.

Concentration of Inhibitor (g/I)	Initial temp. (°C)	Final temp. (⁰ C)	Time (minutes)	Reaction Number	Reaction Number	IE
Concentration of minibitor (g/L)	Ti	T _m t Rn _{wi} F		Rn _{aq}	%	
BLANK	30	55	34	-	0.735	-
1	30	46	35	0.457	0.735	37.80
2	30	45	38	0.395	0.735	46.29
3	30	41	40	0.275	0.735	62.59
4	30	39	43	0.209	0.735	71.52
5	30	37	50	0.140	0.735	80.95
6	30	35	54	0.093	0.735	87.40



Fig. 5: Langmuir adsorption isotherm plot for the adsorption of different concentrations of Mentha spicata extract on the surface of mild steel in 2M HCl solution for 6 hrs at various temperatures.

Thermometric measurement

Corrosion rate and inhibition efficiency were also determined by using the thermometric method. In this method temperature changes in both inhibited and uninhibited mediums were recorded. The results showed that the reaction number decreases as the concentration of

3370

the inhibitor increases which meant inhibition efficiency increases (Table 4). The relation between reaction number and inhibitor concentration shows the variation between reaction number (R.N.) and concentration of the extracts in 2M HCl, denoting that the (R.N.) decreases on increasing the extract concentration. The plot of temperature versus time for the corrosion reaction of mild steel in 2M HCl solution in the absence and presence of different concentrations of Mentha spicata plant extract is depicted in Fig. 6. Inspection of the figure revealed that the dissolution of mild steel begins after a time lag from the immersion of the coupons in the test solution. The time lag may be attributed to the 'incubation period' as observed in HCl medium [38]. Due to the continuous evaluation of hydrogen gas accelerate the corrosion reaction in the acidic medium, the temperature of the system rises gradually due to the exothermic corrosion reaction to reach a maximum value, T_m (55°C). The plot of temperature versus time for the corrosion reaction of mild steel in 2M HCl solution in the absence and presence of different concentrations of Mentha spicata plant extract using thermometric technique is depicted in Fig. 6. The highest inhibition efficiency (87.40% at 303K) obtained by the thermometric method is given in Fig. 7.



Fig. 6: Temperature-time curves for mild steel in different concentrations of HCl solution at $Ti = 30^{\circ}C$.

Quantum chemical calculations

To investigate the effect of electronic structure on the efficiency of inhibitor molecules 3-Penten-2-one, 4-(2,2,6-...1.0]hept-1-yl)-, (E) (PC1) and Stigmast-4-en-3-one (PC2) quantum chemical calculations were carried out. The optimized structures, HOMO and LUMO of the major molecules PC1 and PC2 are shown in Fig. 8 which shows the electron density distribution of HOMO and LUMO orbital are mainly located on heteroatoms for both the molecules. Table 5 constitutes the results of various electronic parameters such as E_{HOMO} , E_{LUMO} , ΔE , dipole moment (μ), and total energy. The propensity of the *PC1* and PC2 molecules to donate electrons is indicated by the energy of HOMO and LUMO orbital. According to the FMO theory of chemical reactivity, the energy of HOMO indicates the tendency of an organic molecule to donate the electrons and the energy of LUMO suggests the tendency to accept the electrons from corresponding metal atoms [37,39]. In Table 5 the high value of E_{HOMO} indicates the higher inhibition efficiency of both selected compounds PC1 and PC2.

 ΔE (energy gap $\Delta E = E_{LUMO} - E_{HOMO}$) is an important parameter as a function of the reactivity of the inhibitor molecule towards the adsorption on the metallic surface. The extent of the lower value of ΔE decreases, the reactivity of the molecule increases leading to better inhibition efficiency, and the removal of an electron from the last occupied orbital will be low [40]. In the present study, the values of ΔE shown in Table 5 indicate that *PC2* has the lowest energy gap 0.7028 (eV) compared to *PC1* molecule, which means that the molecule could have better performance as a corrosion inhibitor.





Fig. 7: Inhibition efficiency- Concentration of inhibitor curve for mild steel in HCl solution at $T_i = 30^{\circ}C$.

The sum of all the energies of the molecule is called total energy. The molecule with the lowest total energy value as a numerical value, the molecule has the highest stability [41]. The calculations indicate that PC2 has total energy (-32581.81), showing its high stability over the other molecules.

The dipole moment (μ) is another important parameter; it can be applied to discuss the molecule structure of the inhibitors and measure of polarity of a polar covalent bond. The high value of the dipole moment pointed to increasing the adsorption of the compounds on the metal [42]. In the present study, the value of dipole moment for phyto constituents (*PC1* and *PC4*) is 5.1014, and 9.2464 Debye respectively, which is higher than that of H₂O (μ =1.85 D). The high dipole moment value of these compounds indicates strong dipole–dipole interactions between molecules and metallic surfaces [41,43,44]. The values of dipole moment pointed to better inhibition efficiency. The possible mode of interaction of selected molecules on the mild steel surface in an acidic medium is given in Fig. 9.

Surface morphology

SEM photographs of mild steel specimens corroded during 6 hour immersion period in the presence and absence of *Mentha spicata* extract in 2M HCl medium at 303K are shown in Fig. 10. Several pits observed in the figure are due to the attack of a corrosive medium on the metal surface in the absence of *Mentha spicata* extract. In the presence of without inhibitor, it can be seen that corroded substrate has micro-cracks and porous structure which shows the non-protective nature of them. On the other hand, In the presence of *Mentha spicata* extract

Quantum chemical parameters	3-Penten-2-one,4-(2,2,6-Trimethyl-7-Oxabicyclo[4.1.0]hept-1-YL)-, (E)- (PC1)	Stigmast-4-en-3-one (PC2)
E _{HOMO} (eV)	-8.4869	-6.6573
E _{LUMO} (eV)	-5.4567	-5.9544
ΔE (L-H) (eV)	3.0302	0.7028
Dipole Moment (µ) Debye	5.1014	9.2464
Total Energy (eV)	-18854.73	-32581.81

Table 5: Calculated quantum chemical parameters for the selected phytochemical constituents presents in Mentha spicata extract.



Fig. 8: Optimized structure and Frontier molecular orbital density distributions (HOMO and LUMO) (a) 3-Penten-2-one,4-(2,2,6-Trimethyl-7-Oxabicyclo[4.1.0]hept-1-YL)-, (E)- (PC1) (b) Stigmast-4-en-3-one (PC2).



Fig. 9: Possible mode of interaction of selected phytoconstituent molecules on the mild steel surface in an acidic medium.



Fig. 10: Scanning Electronic Microscopy (SEM)—images of Mild Steel surface (A)Mild Steel (B) MS in HCl Solution (C) MS in the presence of Inhibitor.

Fig. 10(C) the steel specimen is covered with a layer of inhibitor, which protects the surface from attack of aggressive medium and decreases the rate of corrosion, being responsible for the inhibition [5]. The Comparative study of corrosion inhibition efficiency of some plant extract was reported in the literature by different researchers with the performance of our work as given in Table 6.

CONCLUSIONS

The major phytochemical constituents present in the plant extract have exhibited promising inhibition efficiency for mild steel in 2M HCl. The inhibition efficiency increases with increasing the concentration and decreases with raising the temperature. The degree of surface coverage decreases as temperature increases in acidic environments for the weight loss method considered. The maximum inhibition efficiency observed 86.01% at 6g/L. The adsorption of inhibitor molecules on the metal surface follows Langmuir adsorption isotherm. The inhibition efficiencies obtained from gravimetric and thermometric measurements are in very good agreement. The negative values of ΔG_{ads} show spontaneous adsorption of inhibitor molecules on the metal surface. The theoretical DFT Calculation was in good agreement with the experimental results.

Acknowledgment

I would like to thank Abdeslam El Assyry Laboratoire d'Optoélectronique et de Physico-chimie des Matériaux, (Unité associée au CNRST), Université Ibn Tofail, Faculté des Sciences, B.P. 133, Kénitra, Morocco for quantum

S. No.	Species	Metal	Medium	Methods	%IE	References
1	Mentha spicata Steel 1M HCl Weight los Essential Oil Steel 1M HCl Height los		Weight loss tests, Rp, polarisation and EIS measurements	97	M. Znini 2011	
2	Elephant grass (Pennisetum purpureum)	Mild steel	1M HCl	Weight loss measurement, Atomic adsorption spectrometric analysis	95	K.K. Alaneme 2016
3	Nicotiana tabacum	Mild steel	1M HCl	Gravimetric experiments, Electrochemical measurements	89	D.I. Njokua 2013
4	Punica Plant extract	Carbon steel	1M HCl	Electrochemical measurements, Electrochemical impedance spectroscopy (EIS) measurements	91	Fouda 2014
5	Xanthium strumarium	Carbon steel	1M HCl	Weight loss method	94.82	Khadom 2017
6	Mentha spicata	Mild Steel	2M HCl	Weight loss method, Thermometric method	86.0	This work

 Table 6: Comparison of the %IE of some green corrosion inhibitors with those for Mentha spicata.

chemical studies. The author is also grateful to Dr. D.M. Phase Centre Director (officiate) & Scientist-H, UGC-DEC Consortium for Scientific Research, Indore for providing testing facilities.

Received : Jul. 9, 2022 ; Accepted : Nov. 16, 2022

REFERENCES

- Prabhu R.A., Venkatesha T.V., Shanbhag A.V., Kulkarni G.M., Kalkhambkar R.G., Inhibition Effects Of Some Schiff's Bases on the Corrosion of Mild Steel in Hydrochloric Acid Solution., *J. Corrosion Science*, **50**: 3356-3362 (2008).
- [2] Majidi L., Znini M., Cristofari G., Ansari A., Bouyanzer A., Paolini J., Costa J., Hammouti B., Green Approach to Corrosion Inhibition of Mild Steel by Essential Oil Leaves of Asteriscus Graveolens (Forssk.) in Sulphuric Acid Medium, Int. J. Electrochem. Sci., 7: 3959-3981 (2012).
- [3] Khadom A.A., Ahmed N.A., Nagham A.A., *Xanthium strumarium* leaves Extracts as a Friendly Corrosion Inhibitor of Low Carbon Steel in Hydrochloric Acid: Kinetics and Mathematical Studies, S. Afr. J. Chem. Eng., 25: 13-21 (2018).
- [4] Matjaz F., Jennifer J., Application of Corrosion Inhibitors for Steels in Acidic Media for the Oil and Gas Industry: A Review, *Corros. Sci.*, 86: 17–41 (2014).
- [5] Díaz-Cardenas M.Y., Valladares-Cisneros M.G., Lagunas-Rivera S., Salinas-Bravo V.M., Lopez-Sesenes R., Gonzalez-Rodríguez J.G., *Peumus boldus* Extract as Corrosion Inhibitor for Carbon Steel in 0.5 M Sulfuric Acid, *Green Chem. Lett. Rev.*, **10**: 257–268 (2017).

- [6] Alaneme K.K., Olusegun S.J., Alo A.W., Corrosion Inhibitory Properties of Elephant Grass (*Pennisetum purpureum*) Extract: Effect on Mild Steel Corrosion in 1M HCl Solution, *Alexandria Eng. J.*, 55: 1069– 1076 (2016)
- [7] Olajire A.A., Corrosion Inhibition of Offshore Oil and Gas Production Facilities Using Organic Compound Inhibitors - A Review, J. Mol. Liq., 248: 775–808 (2017)
- [8] Samiee R., Ramezanzadeh B., Mahdavian M. Alibakhshi E., Assessment of the Smart Self-Healing Corrosion Protection Properties of a Water-Base Hybrid Organo-Silane Film Combined with Non-Toxic Organic/Inorganic Environmentally Friendly Corrosion Inhibitors on Mild Steel, J. Clean Prod., 220: 340-356 (2019).
- [9] Radojc'ic' I., Berkovic' K., Kovac' S., Vorkapic'-Furac' J., Natural Honey and Black Radish Juice as Tin Corrosion Inhibitors, *Corros. Sci.*, **50**: 1498–1504 (2008).
- [10] Bhawsar J., Jain P.K., Jain P., Experimental and Computational Studies of Nicotiana Tabacum Leaves Extract as Green Corrosion Inhibitor for Mild Steel in Acidic Medium, *Alexandria Eng. J.*, 54: 769–775 (2015)
- [11] Umoren S.A., Solomon M.M., Obot I.B., Sulieman R.K., A Critical Review on the Recent Studies on Plant Biomaterials as Corrosion Inhibitors for Industrial Metals, J. Ind. Eng. Chem., 76: 91-115 (2019).
- [12] Sukul D., Pal A., Mukhopadhyay S., Saha S.K., Banerjee P., Electrochemical Behaviour of Uncoated and Phosphatidylcholine Coated Copper in Hydrochloric Acid Medium, J. Mol. Liq., 249: 930– 940 (2018)

- [13] Umoren S.A., AlAhmary A.A., Gasem Z.M., Solomon M.M., Evaluation of Chitosan and Carboxymethyl Cellulose as Ecofriendly Corrosion Inhibitors for Steel, Int. J. Biol. Macromol., 117: 1017–1028 (2018)
- [14] Umoren S.A., Solomon M.M., Obot I.B. Sulieman R.K., A Critical Review on the Recent Studies on Plant Biomaterials as Corrosion Inhibitors for Industrial Metals, J. Ind. Eng. Chem., 76: 91-115 (2019).
- [15] Krishnaveni K., Ravichandran J. and Selvaraj A., Effect of *Morinda tinctoria* Leaves Extract on the Corrosion Inhibition of Mild Steel in Acid Medium, Acta Metall. Sin., 6: 321-327 (2003).
- [16] Zucchi F., Plant Extracts as Corrosion Inhibitors of Mild Steel in HCI Solutions, Surf. Technol., 24: 391– 399 (1985).
- [17] Wang X., Jiang H., Zhang D., Hou L., Zhou W., Solanum lasiocarpum L. Extract as Green Corrosion Inhibitor for A3 Steel in 1M HCl Solution, Int. J. Electrochem. Sci., 14: 1178 – 1196 (2019).
- [18] Belarbi N., Dergal F., Chikhi I., Merah S., Lerari D., Bachari K., Study of Anti-Corrosion Activity of Algerian L. Stoechas Oil on C38 Carbon Steel in 1 M HCl Medium, Int. J. Ind. Chem., 9: 115-125 (2018).
- [19] Fouda A.S., Etaiw H.S., Elnggar W., Punica Plant Extract as Green Corrosion Inhibitor for C-Steel in Hydrochloric Acid Solutions, Int. J. Electrochem. Sci., 9: 4866 – 4883 (2014).
- [20] Dhaundiyal P., Bashir S., Sharma V., Kumar A., An Investigation on Mitigation of Corrosion of Mild steel by Origanum vulgare In Acidic Medium, *Bull. Chem. Soc. Ethiop.*, **33(1)**: 159-168 (2019).
- [21] Snoussi M., Noumi E., Trabelsi N., Flamini G., Papetti A., De Feo V., Mentha spicata Essential Oil: Chemical Composition, Antioxidant and Antibacterial Activities Against Planktonic and Biofilm Cultures of Vibrio spp. Strains, *Molecules*, 20: 14402-14424 (2015).
- [22] Jain P.K., Soni A., Jain P., Bhawsar J., Phytochemical Analysis of Mentha Spicata Plant Extract Using UV-VIS, FTIR and GC/MS Technique, J. Chem. Pharma. Res., 8: 1-6 (2016).
- [23] Deepa Rani P., Selvaraj S., Inhibitive action of *Vitis vinifera* (Grape) on Copper and Brass in Natural Sea Water Environment, *Rasayan J. of Chemistry*, 3: 473-482 (2010).

- [24] ASTM, American Society for Testing and Materials, Philadelphia, G 31-72, PA (1990).
- [25] Ebenso E.E., Eddy N.O., Odiongenyi A.O., Corrosion Inhibitive Properties and Adsorption Behaviour of Ethanol Extract of *Piper guinensis* as a Green Corrosion Inhibitor for Mild Steel in H2SO4. *Afr. J. Pure Appl. Chem.*, 2: 107-115 (2008).
- [26] Murmu M., Saha S. Kr., Murmu N.C., Banerjee P., Effect of Stereochemical Conformation into the Corrosion Inhibitive Behaviour of Double Azomethine Based Schiff Bases on Mild Steel Surface In 1 Mol L-1 Hcl Medium: An Experimental, Density Functional Theory and Molecular Dynamics Simulation Study, *Corros. Sci.*, **146**: 134-151 (2019).
- [27] Verma C., Lgaz H., Verma D.K., Ebenso E.E., Bahadur I., Quraishi M.A., Molecular Dynamics and Monte Carlo Simulations as Powerful Tools for Study of Interfacial Adsorption Behavior of Corrosion Inhibitors in Aqueous Phase: A Review, J. Mol. Liq., 260: 99–120 (2018).
- [28] Bhawsar J., Jain P., Valladares-Cisneros M.G., Cuevas-Arteaga C., Bhawsar M.R., Quantum Chemical Assessment of Two Natural Compounds: Vasicine and Vasicinone as Green Corrosion Inhibitors, Int. J. Electrochem. Sci., 13: 3200 – 3209 (2018).
- [29] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Petersson G.A., Nakatsuji H., Li X., Caricato M., Marenich A., Bloino J., Janesko B.G., Gomperts R., Mennucci B., Hratchian H.P., Ortiz J.V., Izmaylov A.F., Sonnenberg J.L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V.G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Montgomery J.A., Jr., Peralta J.E., Ogliaro F., Bearpark M, Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Keith T., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Millam J.M., Klene M., Adamo C., Cammi R., Ochterski J.W., Martin R.L., Morokuma K., Farkas O., Foresman J.B., and Fox D.J., 2016 Gaussian, Inc., Wallingford C.T., Gaussian 09, Revis. A. 02. (2009).

- [30] Nikpour S., Ramezanzadeh M., Bahlakeh G., Ramezanzadeh B., Mahdavian M., Eriobotrya Japonica Lindl Leaves Extract Application for Effective Corrosion Mitigation of Mild Steel in HCl Solution: Experimental and Computational Studies, *Constr. Build. Mater.*, **220**: 161–176 (2019).
- [31] Njokua D.I., Chidiebere M.A., Oguzie K.L., Ogukwe C.E., Oguzie E.E., Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution by the Leaf Extract of *Nicotiana tabacum*, Adv. Mater. Corros., 1: 54-61 (2013).
- [32] Liang Y., Wang C., Li J., Wang L.J., Jia J.F., The Penicillin Derivatives as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution: Experimental and Theoretical Studies, *Int. J. Electrochem. Sci.*, 10: 8072 – 8086 (2015).
- [33] Bhawsar J., Jain P.K., Jain P., Soni A., Anticorrosive Activity of *Glycine max* (L) Oil against the Corrosion of Mild Steel in Acidic Medium, *Int. J. Res. Chem. Environ.*, 3: 68-74 (2013).
- [34] Jafari H., Akbarzade K., Effect of Concentration and Temperature on Carbon Steel Corrosion Inhibition, *Journal of Bio-and Tribo-Corrosion*, **3**: 8–14 (2017).
- [35] Rodríguez Torres A., Valladares Cisneros M.G., González Rodríguez J.G., *Medicago sativa* as a Green Corrosion Inhibitor for 1018 Carbon Steel in 0.5 M H2SO4 Solution, *Green Chem. Lett. Rev.*, 9: 143–155 (2016).
- [36] Ojha L.K., Kaur K., Kaur R., Bhawsar J., Corrosion Inhibition Efficiency of Fenugreek Leaves Extract on Mild Steel Surface in Acidic Medium, J. Chem. Pharma. Res., 9: 57-64 (2017)
- [37] Jafari H., Danaee I., Eskandari H., RashvandAvei M., Electrochemical and Theoretical Studies of Adsorption and Corrosion Inhibition of N,N'-Bis(2hydroxyethoxyacetophenone)-2,2-dimethyl-1,2propanediimine on Low Carbon Steel (API 5L Grade B) in Acidic Solution, *Industrial & Engineering Chemistry Research*, 52(20): 6617–6632 (2013).
- [38] Ali A.I., Megahed H.E., Elsayed M. and El-Etre A.Y., Inhibition of Acid Corrosion of Aluminum Using Salvadore Persica. J. Environ. Sci., 1: 136-147 (2014)
- [39] Ladha D.G., Shah N.K., Ghelichkha Z., Obot I.B., Dehkharghani F.K., Yao J.Z., Macdonald D.D., Experimental and Computational Evaluation of Illicium Verum as a Novel Eco-Friendly Corrosion Inhibitor for Aluminium, *Mater. Corros.*, 69: 1-15 (2017).

- [40] Li X., Deng S., Fu H., Li T., Adsorption and Inhibition Effect of 6-benzylaminopurine on Cold Rolled Steel in 1.0 M HCl, *Electrochim. Acta*, 54: 4089–4098 (2009).
- [41] Padash R., Mehdi R.N., Ali S.R., Ali S.N., Jesionowski T., Ehrlich H., A theoretical Study of Two Novel Schiff Bases as Inhibitors of Carbon Steel Corrosion in Acidic Medium, *Appl. Phys.* A, **125**: 1-11 (2019).
- [42] Gece G., The Use of Quantum Chemical Methods in Corrosion Inhibitor Studies, Corros. Sci., 50: 2981-2992 (2008).
- [43] Zarrok H., Oudda H., Zarrouk A., Salghi R., Hammouti B., Bouachrine M., Weight Loss Measurement and Theoretical Study of New Pyridazine Compound as Corrosion Inhibitor for C38 Steel in Hydrochloric Acid Solution, *Der pharma Chem.*, **3**: 576-590 (2011)
- [44] Al-Amiery A., Salman T.A., Alazawi K.F., Shaker L.M., Kadhum A.A.H., Takriff Md. S., Quantum Chemical Elucidation on Corrosion Inhibition Efficiency of Schiff Base: DFT Investigations Supported by Weight Loss and SEM Techniques, International Journal of Low-Carbon Technologies, 15(2): 202–209 (2020).