



Electrochemical, computational and adsorption studies of leaf and floral extracts of *Pogostemon quadrifolius* (Benth.) as corrosion inhibitor for mild steel in hydrochloric acid

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Abstract

Pogostemon quadrifolius methanolic leaf extracts (PQML) and floral extracts (PQMF) have been investigated as corrosion inhibitors for mild steel in 1M hydrochloric acid. Corrosion rates were studied at 303K, 313K and 323K by weight loss method at varying inhibitor concentrations. Electrochemical impedance spectroscopy and potentiodynamic polarization techniques were used to study corrosion rate at 303 K in various inhibitor concentrations. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and adsorption studies were used to study the surface morphology and mechanism of corrosion inhibition. EIS data and weight loss data shows maximum inhibition efficiency 95.79 % & 96.5% respectively at 300 ppm inhibitor concentration at 303K for floral extracts and 85 % and 90.5 % for leaf extracts. Moreover floral extracts were found to be more efficient corrosion inhibitor than leaf extracts. To identify the contribution of major components in the inhibition potential of the extracts, computational calculations corresponding to (Z)-ethylidene-4, 6-dimethoxycoumaran-3-one (EDC) and Geranyl vinyl ether (GVE) were carried out. Quantum chemical parameters well explain the effect of structural peculiarities on electron donating ability of EDC and GVE. The surface interaction of both floral and leaf extracts on mild steel was obeying Langmuir adsorption isotherm at all temperatures.

1. Introduction

Corrosion of metals is, though unavoidable, but a controllable process. The National Institute of Standards and Technology has estimated that the annual cost of corrosion in the US was in the range of \$9 billion to \$ 90 billion [1]. In most of the industrialized nations the cost of corrosion has been identified upto 3 -5% of the gross national product [2]. Metals and their alloys which are exposed to adverse conditions during various stages can accelerate degradation. In order to prevent corrosion, methods like water displacing products (oil or grease), water absorption products (silica gel) and dehumidification were employed previously, but they became insignificant due to high material cost for application and removal and high labour [3]. In acidic media, especially in oil and gas industries, the use of inhibitor was found to be the best approach for protecting metals against corrosion. The general corrosion rate may be extremely high and increase exponentially with increasing temperature and acid concentrations, in the absence of corrosion inhibitors [4].

Corrosion inhibitors execute inhibition by protecting the surface of metals either by merging with them or by reacting with the impurities in the environment which may cause pollution [5]. Corrosion inhibitors act in many ways; it may restrict the rate of the cathodic or anodic process by blocking the active sites on the metal surface or

it may increase the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. Further some inhibiting compounds form a thin layer on the surface which stifles the corrosion process [6]. For the protection of steel in acidic media, organic corrosion inhibitors are more effective than inorganic compounds [5]. Environmental damage due to inorganic inhibitors and toxicity due to organic inhibitors resulted in the use of ecofriendly green inhibitors. Non toxic, biodegradable green inhibitors from different plant parts has been proven as good corrosion inhibitors as revealed in literature [7-20]. Various factors like nature of metal , chemical structure of inhibitor, presence of additives, testing media, solution temperature , solution concentration etc. influence adsorption of natural corrosion inhibitors on mild steel surface [21].

Plant extracts are rich in compounds like alkaloids, flavonoids, tannins etc., which have the potential to act as corrosion inhibitor. In case of natural products it is difficult to identify the compound which exactly acts against corrosion. In fact it is a synergistic action of several components in a plant extract. Even though it is unknown that which component may act as inhibitor, the major components of a plant extract can also be monitored for its corrosion inhibition property [17].

Pogostemon quadrifolius (Benth.) belonging to family Lamiaceae is a common ethnobotanically important medicinal plant in India and some adjacent countries and is used as a folk medicine against chicken pox worms. It is also a blood purifier [22, 23]. Methanolic stem extracts of *P. quadrifolius* has been reported to show good corrosion inhibition activities for mild steel in 1 M HCl [24]. (Z)- ethylidene-4,6-dimethoxycoumaran-3-one (EDC) was identified and separated as one of the major compound from the leaves of *P. quadrifolius* [25]. Geranyl vinyl ether (GVE) has been identified as the major compound in the methanolic extract of flowers of *P. quadrifolius* [26]. (Z)-ethylidene-4,6-dimethoxycoumaran-3-one and Geranyl vinyl ether (Fig 1 & 2) were analysed in this study for its corrosion inhibition property theoretically. As it won't be cost effective, separation and experimental work using EDC and GVE has not been attempted. With the support of theoretical calculations the potential of the plant as an inhibitor can be best studied [18]. Apart from leaf extracts floral extracts were also studied for corrosion inhibition property using weight loss method, electrochemical impedance spectroscopy, potentiodynamic polarization technique, FT-IR and SEM.

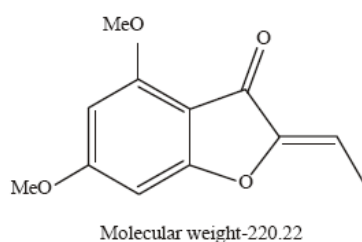


Fig. 1: Structure of (Z)-ethylidene-4, 6-dimethoxycoumaran-3-one (EDC)

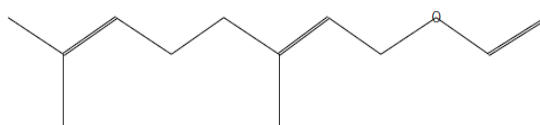


Fig 2: Structure of Geranyl vinyl ether (GVE) MW 180

2. Material and Methods

2.1/ Materials

Mild steel of size $2 \times 1.8 \text{ cm}^2$ were used as test specimens. Only 1 cm^2 area of test specimen was exposed during each measurement in electrochemical experiments. Prior to the measurements the test specimens were rubbed with various grades of emery papers (600 - 1200 grades) and then subjected to the action of a buffing machine with a cotton wheel and a fibre wheel having buffing soap to ensure a mirror- bright finish followed by washing with water and acetone as recommended by ASTM standard G -1-72. Weight of the samples was taken accurately using four digit electronic balance (Shimadzu AAY220). 1 M HCl was prepared from analytical grade HCl (Merck) using double distilled water. The concentration ranges of the inhibitors were 100, 150, 200, 250 and 300 ppm in 1 M HCl.

2.2/ Inhibitor preparation

The fresh flowers and leaves of *P. quadrifolius* were collected from the surrounding areas and were washed, shade dried and made into fine powder using a mixer grinder and the powder was kept in small airtight bottles with proper labelling. Powdered flowers and leaves were extracted using methanol in soxhlet apparatus, until all the constituents were completely eluted. The filtered and evaporated dry extracts were used as the corrosion inhibitor.

2.3/ Gravimetric measurements

The pre- weighed steel samples were immersed in blank solution of 1 M HCl and also in 50 ml 1M HCl solution containing different concentrations of inhibitor (100 ppm, 150ppm, 200 ppm, 250 ppm and 300 ppm) for 6 hours. Gravimetric measurements were carried out at 303 K, 313 K and 323K temperatures. The withdrawn steel specimens were carefully rinsed with double distilled water, cleaned with acetone, dried at room temperature and weighed.

2.4/ Electrochemical measurements

Electrochemical measurements were carried out by the method described in literature [17,18] using Gill AC computer controlled work station. A conventional three – electrode cell assembly with thermostatically controlled temperature (303 K) was used for electrochemical studies. Working electrode (WE) was the pure mild steel specimen, counter electrode was the platinum electrode and reference electrode, the saturated calomel electrode (SCE). Electrochemical impedance spectroscopy was carried out imposing sinusoidal voltage of 10 mV amplitude at a frequency range 10 kHz to 0.1 Hz to determine the corrosion inhibition efficiency of PQ extracts. The inhibition efficiency was calculated with the equation

$$IE (\%) = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} \times 100 \quad (1)$$

where R_{ct}^* and R_{ct} are the charge transfer resistances with and without inhibitor respectively.

Information regarding corrosion potential and corrosion current density which is directly proportional to corrosion rate was provided by polarisation technique. By extrapolating the linear segments of anodic and cathodic polarization curves (Tafel extrapolation method) to corrosion potential (E_{corr}) at different inhibitor concentrations, corrosion current density (i_{corr}) was obtained. The impedance diagrams are provided in the form of Nyquist plots. The charge transfer resistance values were identified from the diameter of the semicircles of the Nyquist plots. The corrosion inhibition efficiency was evaluated from the measured i_{corr} values as,

$$IE (\%) = \frac{i_{corr} - i_{corr}^*}{i_{corr}} \times 100 \quad (2)$$

where i_{corr} and i_{corr}^* are corrosion current densities without and with the inhibitor respectively.

2.5/ Computational studies

Full geometry optimization of the inhibitors were performed using DFT (density functional theory) with Beck's three –parameter exchange functional along with Lee-Yang - Par non local correlation functional (B3LYP) with 6-311 G (d,p) basic set using the Gaussian 09 programme package. Energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), ΔE (HOMO – LUMO energy gap), dipole moment (μ), total energy (TE), electronegativity (χ), hardness (η), the number of transferred electrons (ΔN) etc. are identified.

3. Results and discussion

3.1/ Weight loss technique

Though weight loss method is the easiest regarded as 'gold standard' corrosion testing, the sensitivity of this method is very limited as weight can be measured only to about 0.1 mg. The weight loss measurement results conducted at 303 K, 313K and 323 K for floral and leaf extracts are provided in tables 1 & 2. It can be noted that with increasing inhibitor concentration the inhibition efficiency percentage increased which was estimated as

$$\text{Inhibition efficiency (IE \%)} = [(W_1 - W_2) / W_1] \times 100 \quad [3]$$

where W_1 was weight loss without inhibitor and W_2 weight loss with inhibitor and corrosion rate as

$$\text{Corrosion rate (C}_R) = (W_b - W_a) / A t \quad [4]$$

where W_a and W_b are the weight of steel specimens after and before immersions in the corrosion media, A the area of steel specimen in cm^2 , t the time of exposure in hours.

Table 1. Corrosion parameters of mild steel in the absence and presence of PQMF

Temperature	Concentration of plant extract in 1M HCl (ppm)	Weight of steel before immersion	Weight of steel after immersion	Weight loss	wb-wa	Corrosion rate (CR in $\text{g}/\text{cm}^2\text{h}$)	Inhibition Efficiency (IE %)
303K	Blank	3.26	3.19	0.07		3.162	
	100	3.26	3.25	0.01	0.062	0.459	85.5
	150	3.25	3.24	0.01	0.064	0.357	88.7
	200	3.59	3.58	0.01	0.066	0.275	91.3
	250	3.24	3.23	0.01	0.067	0.206	93.5
	300	3.47	3.46	0.01	0.070	0.111	96.5
313K	Blank	3.78	3.67	0.11		5.031	
	100	3.85	3.83	0.02	0.096	0.826	83.6
	150	3.47	3.45	0.02	0.099	0.689	86.3
	200	3.21	3.20	0.01	0.103	0.528	89.5
	250	3.75	3.74	0.01	0.105	0.418	91.7
	300	3.74	3.73	0.01	0.108	0.292	94.2
323K	Blank	3.74	3.60	0.14		6.263	
	100	3.26	3.23	0.03	0.117	1.134	81.9
	150	3.78	3.76	0.02	0.120	0.965	84.6
	200	3.69	3.68	0.01	0.125	0.802	87.2
	250	3.25	3.24	0.01	0.128	0.658	89.5
	300	3.54	3.53	0.01	0.132	0.482	92.3

Table 2. Corrosion parameters of mild steel in the absence and presence of PQML

Temperature	Concentration of plant extract in 1M HCl (ppm)	Weight of steel before immersion	Weight of steel after immersion	Weight loss	wb-wa	Corrosion rate (CR in $\text{g}/\text{cm}^2\text{h}$)	Inhibition Efficiency (IE %)
303K	Blank	3.26	3.19	0.07		3.162	
	100	3.26	3.24	0.02	0.054	0.784	75.2
	150	3.69	3.67	0.02	0.057	0.619	80.4
	200	3.48	3.46	0.02	0.061	0.490	84.5
	250	3.79	3.78	0.01	0.063	0.386	87.8
	300	3.97	3.96	0.01	0.065	0.300	90.5
313K	Blank	3.78	3.67	0.11		5.031	
	100	3.25	3.22	0.03	0.084	1.338	73.4
	150	3.25	3.22	0.03	0.090	1.097	78.2
	200	3.68	3.66	0.02	0.094	0.890	82.3
	250	3.46	3.44	0.02	0.098	0.714	85.8
	300	3.25	3.23	0.02	0.101	0.599	88.1
323K	Blank	3.74	3.60	0.14		6.263	
	100	3.25	3.21	0.04	0.103	1.766	71.8
	150	3.66	3.62	0.04	0.110	1.459	76.7
	200	3.89	3.86	0.03	0.114	1.284	79.5
	250	3.25	3.22	0.02	0.120	1.033	83.5
	300	3.74	3.72	0.02	0.123	0.864	86.2

3.2. /Electrochemical Impedance Spectroscopic (EIS) studies

The Nyquist plots which has been obtained from EIS studies has been provided in figures 3 & 4. Due to surface inhomogeneity, roughness or impurities or dislocations, [27, 28, 17] the Nyquist plots are not perfect semicircles. The impedance spectra shows a single semicircle for a particular PQ concentration. The diameter of the capacitive loop in the presence of PQ extracts is larger than in the blank solution and diameter of Nyquist plots were found increasing with increase in concentration of PQ extracts which resulted in strengthening the inhibitive film. EIS result (Table 3) also shows that R_{ct} value increases with increasing inhibitor concentration indicating that the mild steel surface is protected by the inhibitor. The maximum IE in PQ extracts reaches more than 90% and these results are in agreement with those obtained from polarisation studies.

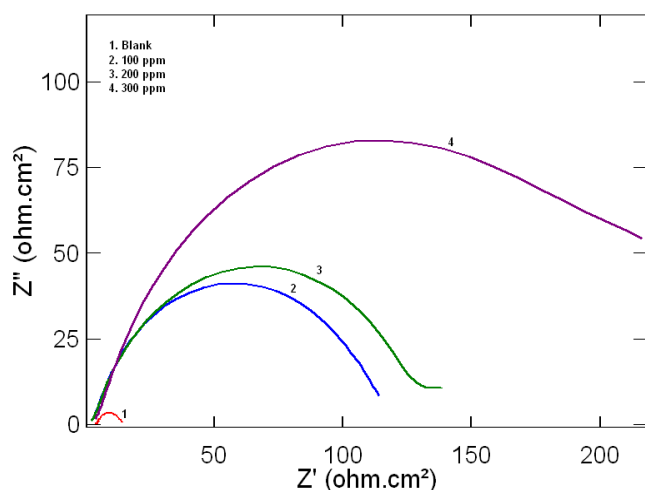


Fig. 3. Nyquist plot for mild steel PQMF

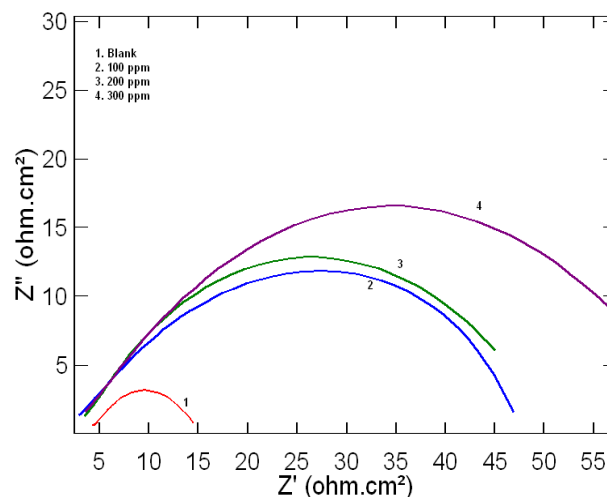


Fig. 4. Nyquist plot for mild steel PQML

Table 3. EIS data for mild steel in 1 M HCl without and with extracts of leaves and flowers of PQ

Sample	Concentration (ppm)	$R_{ct}(\Omega \text{ cm}^2)$	$I_{corr} (\text{mAcm}^2)$	$C_r (\text{mm/yr})$	IE %
Blank	-----	9.256	2.818	32.67	-----
PQML	100	45.52	0.573	6.642	79.66
	200	47.91	0.545	6.31	80.68
	300	61.71	0.423	4.899	85.00
PQMF	100	112.00	0.233	2.700	91.73
	200	129.30	0.202	2.338	92.84
	300	220.20	0.119	1.373	95.79

3.3./Potentiodynamic polarization studies

The inhibition of various extracts of PQ on mild steel specimens in 1 M HCl were investigated by measuring the anodic and cathodic behavioural changes of the specimens which is corresponding to metal oxidation and hydrogen reduction. The anodic and cathodic potentiodynamic polarization curves of carbon steel in 1 M HCl without and with varying concentrations of samples of various extracts of PQ were recorded at a scanning rate of 1 mV s^{-1} at room temperature (303 K) are represented in figures 5 & 6. In table 4 electrochemical parameters determined from polarisation curves as corrosion potential (E_{corr}), anodic and cathodic Tafel constants (β_a and β_c), corrosion current density (I_{corr}) and corrosion rate are given. From these polarisation results it is clear that the I_{corr} values decrease considerably in the presence of PQ extracts with increasing concentrations from 100 – 300 ppm. Inhibition efficiency increases with increasing extract concentration, reaching 87.20 % and 95.10 % respectively in leaves and flowers of PQ. The addition of PQ extracts in HCl slightly modifies the Tafel slopes. In the presence of various concentrations of PQ extracts in 1M HCl, no definite trend was observed in the shift of E_{corr} values. These observations indicate that PQ exhibits cathodic and anodic inhibition effects showing mixed type of inhibition behaviour in 1 M HCl. Generally if the displacement in corrosion potential is more than 85mV with respect to corrosion potential of blank, the inhibitor may be cathodic or anodic type.

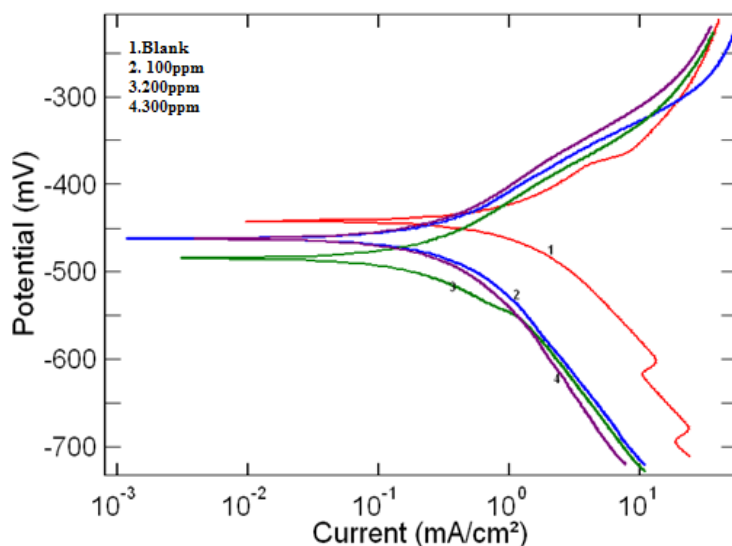


Fig : 5. Polarization curves for mild steel PQML

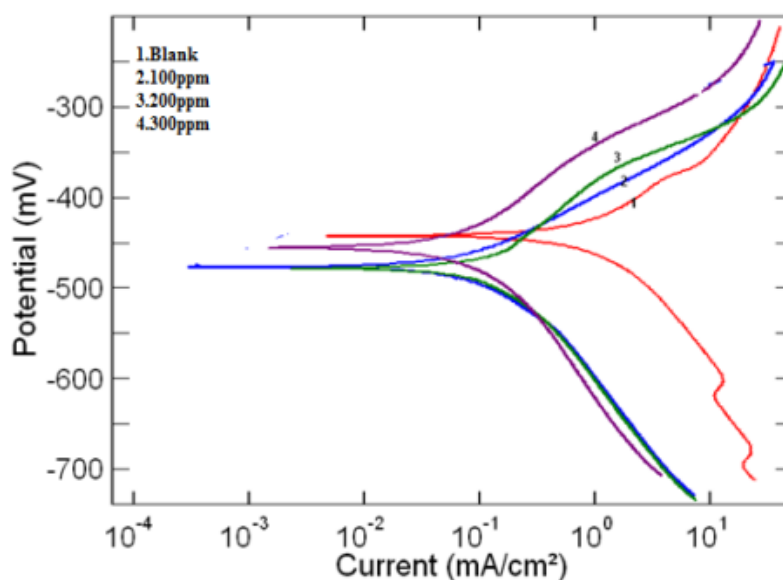


Fig : 6. Polarization curves for mild steel PQMF

Table 4. Polarisation data for mild steel in 1 M HCl without and with extracts of different parts of PQ for 1 hr

Sample	Concentration of inhibitor (ppm)	E_{corr} (mV)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	I_{corr} (mA cm ²)	C_r mm/yr	IE %
Blank		-443	117	173	1.662	19.262	
PQML	100	-461	97.00	126	0.460	5.333	72.30
	200	-483	101	118	0.305	3.539	81.60
	300	-464	92.00	108	0.212	2.454	87.20
PQMF	100	-474	79.00	154	0.155	1.797	90.60
	200	-478	77.00	127	0.131	1.521	92.10
	300	-455	85.54	125	0.081	0.934	95.10

Based on the results obtained from electrochemical studies it can be concluded that the IE increases gradually with addition of each 100 ppm of the extract upto the highest concentration, and even at the lowest inhibitor concentration, there is considerable IE. Thus, PQ is a good inhibitor against mild steel corrosion in HCl and floral extracts are more efficient inhibitor than leaves.

3.4/ Adsorption studies and thermodynamic parameters

The corrosion inhibition mechanism can be best explained using adsorption isotherms. It provide information regarding the interaction between inhibitor and mild steel surface. The surface coverage values (θ) at different concentrations of inhibitor (PQML & PQMF) in 1M HCl were calculated from weight loss measurements conducted at 303K, 313 K, and 323 K. The frequently used adsorption isotherms are Temkin, Frumkin and Langmuir isotherms. The experimental data was tested on these adsorption isotherms and through correlation coefficient (R^2) usage the best fit was obtained from Langmuir adsorption isotherm (Figs. 7 & 8) which is represented by the equation :

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad [5]$$

where C_{inh} represent the concentration of the inhibitor, K_{ads} is the equilibrium constant of adsorption process and θ , the surface coverage. Figures 7 & 8, show straight lines of C_{inh}/θ against C_{inh} at all studied temperatures. The results show the linear regression coefficient (R^2) and slope close to unity, which confirms the adsorption of both PQ leaf and flower extracts on mild steel surface obeying Langmuir adsorption isotherm.

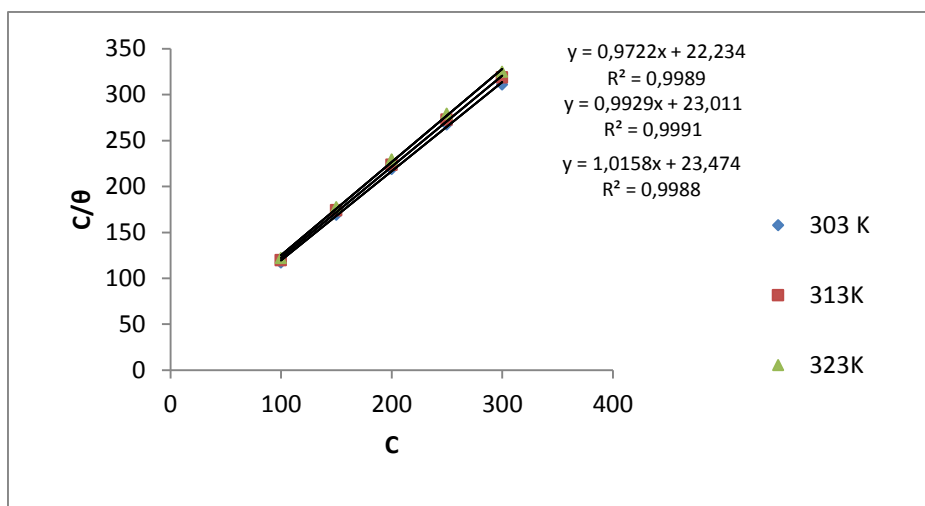


Fig : 7 Langmuir adsorption isotherm for mild steel in 1M HCl for different concentrations of PQMF

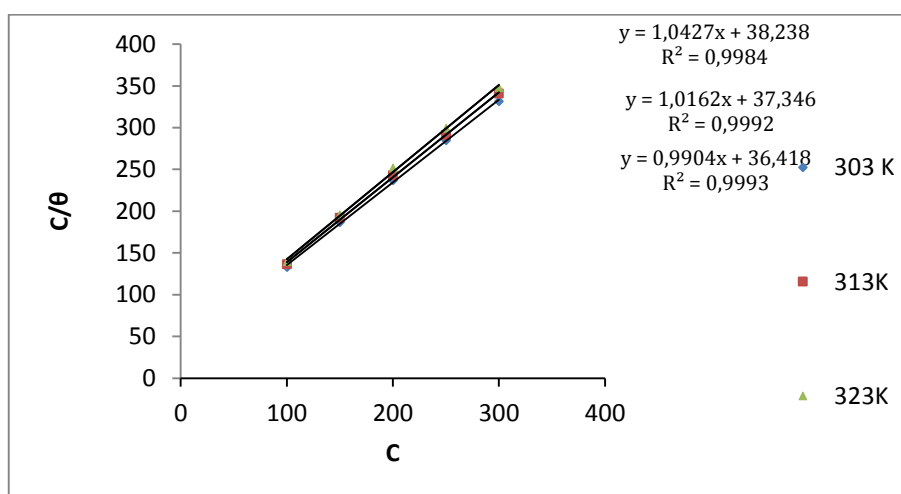


Fig : 8 Langmuir adsorption isotherm for mild steel in 1M HCl for different concentrations of PQML

It is well known that the natural extract contains infinite components at various contents and the majority contains one and/or more than function group as ketone, alcohol, acid, aldehyde..., the inhibitory effect is generally interpreted by the intermolecular synergistic effect of several molecules [29-34]. Also, the concentration is generally expressed by ppm or g/L and not for specific molecule, the determination of adsorption parameters as free enthalpy, enthalpy and/or entropy has no scientific meaning [35-37].

3.5/ Theoretical calculations

Quantum chemical study is an excellent tool in determining the molecular structure, electronic structure as well as reactivity of molecules in corrosion studies [38]. Certain quantum chemical calculations were performed to study the effect of molecular structure on inhibition efficiency using Gaussian 09 programme package. Quantum chemical parameters obtained from the calculations such as the energies of frontier molecular orbitals (E_{HOMO}) and (E_{LUMO}), the separation energy ($E_{\text{HOMO}} - E_{\text{LUMO}}$) (ΔE), representing the function of reactivity, dipole moment (μ), total energy (TE), ΔN representing the fraction of electrons transferred from ligand to metal are collected in table 7.

Electronic structures of the phytochemicals selected in the study, EDC from PQML and GVE from PQMF are illustrated in Fig. 9 & 10., which include optimized geometry, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of EDC & GVE. E_{HOMO} show the electron donating ability of molecules and generally the higher the E_{HOMO} value, the greater the tendency of the molecule to donate electrons to acceptor molecule and the lower the E_{LUMO} value (electron accepting ability of the molecule) the greater the tendency to accept electrons [39,40]. In the case of EDC, E_{HOMO} is -6.257 eV and E_{LUMO} is -1.949 eV and of GVE, E_{HOMO} is -6.12 eV and E_{LUMO} is 0.08 eV. The energy difference between E_{HOMO} and E_{LUMO} , ΔE , indicate the reactivity (inhibition efficiency) of the given compound and generally smaller the ΔE value, the greater will be the efficiency of the molecule [36,39]. The ΔE value of EDC was obtained as 4.308 and of GVE 6.2 both of which are comparatively lower values. The low values of dipole moment is also associated with good inhibition properties [41]. The ionisation energy (I) and electron affinity (A) is related to E_{HOMO} and E_{LUMO} as per below [42, 43].

$$I = - E_{\text{HOMO}} \quad A = - E_{\text{LUMO}} \quad [9]$$

Table 7. Quantum chemical parameters for EDC & GVE

Chemical constituent	Total energy	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	I	A	χ (electro negativity) (eV)	η (global hardness) (eV)	σ (global softness) (eV)	ΔN (eV)	Dipole moment D
EDC	-765.22	-6.257	-1.949	4.308	6.257	1.949	4.103	2.154	0.464	0.672	4.55
GVE	-544.32	-6.12	0.08	6.2	6.12	-0.08	3.019	3.099	0.323	0.6423	1.8

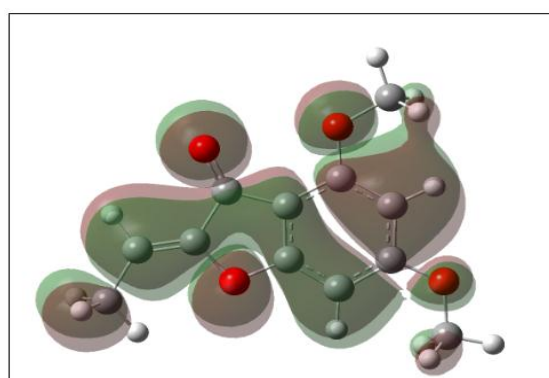


Fig : 9. a. HOMO EDC

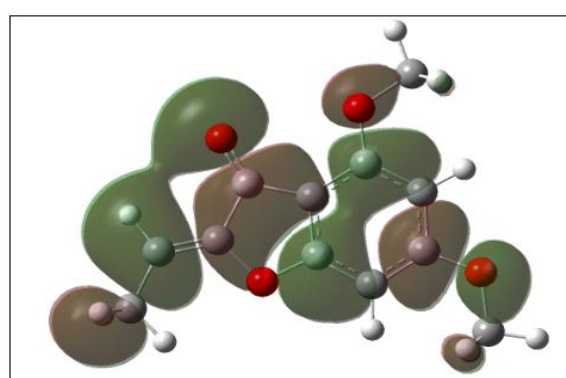


Fig 9.b. LUMO EDC

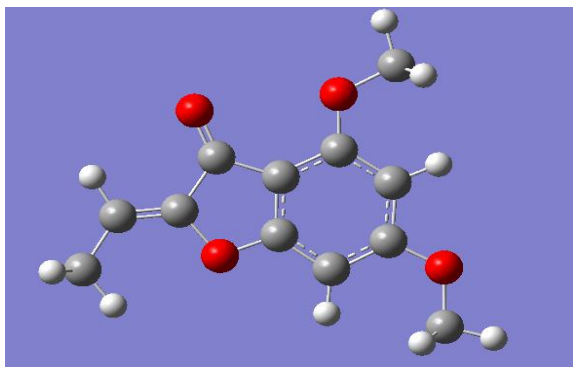


Fig. 9 c. Optimized geometry of EDC

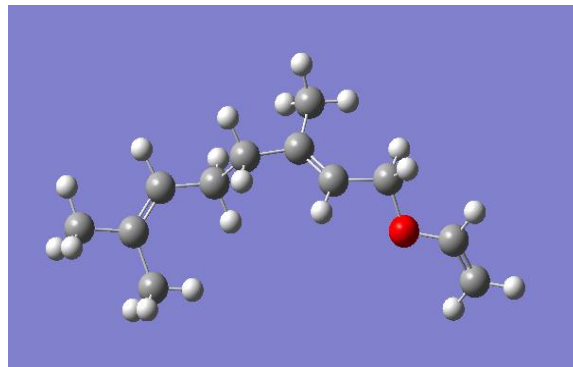


Fig.10a. Optimized geometry of GVE

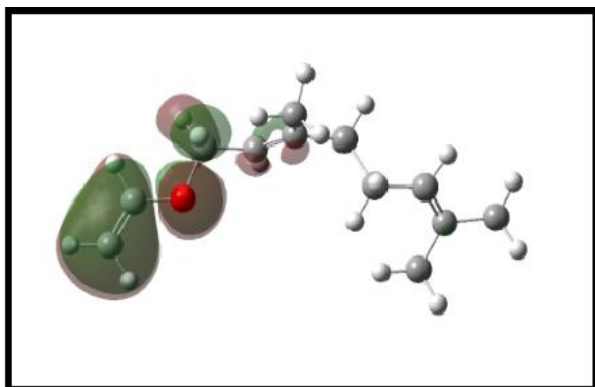


Fig : 10 b. HOMO GVE

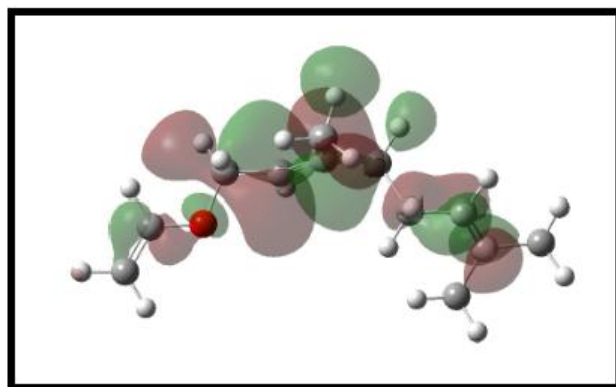


Fig 10.c. LUMO GVE

3.6/ Scanning electron microscopic studies (SEM)

SEM studies were conducted to study the surface morphology of mild steel before and after immersion in 1 M HCl without and with PQML and PQMF extracts (300ppm) and the results obtained are provided in figures 11,12,13 and 14. From the figures it is clear that the extract form a protective film over mild steel specimen and prevent corrosion by acid solution.

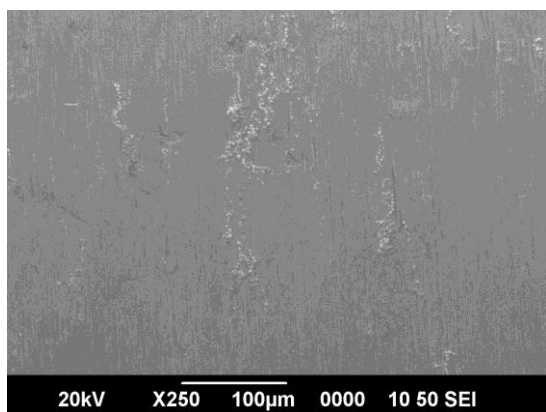


Fig : 11.SEM image of polished mild steel before immersion in test solution

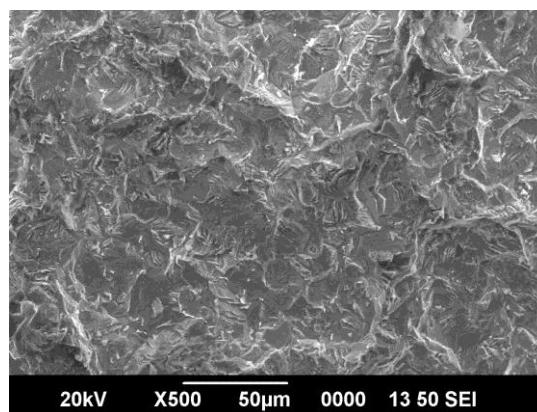


Fig: 12.SEM image of mild steel after immersion in 1M HCl without inhibitor

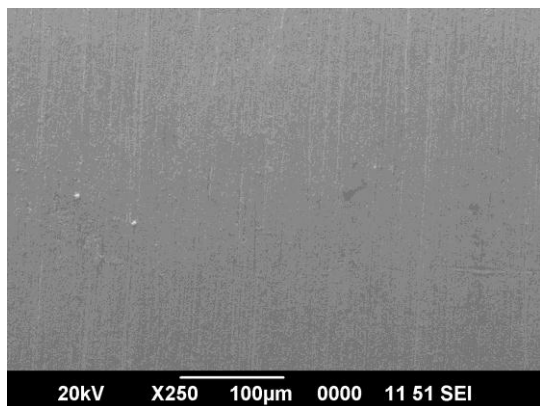


Fig :13. SEM image of mild steel after immersion in 1M HCl with inhibitor PQMF 300ppm

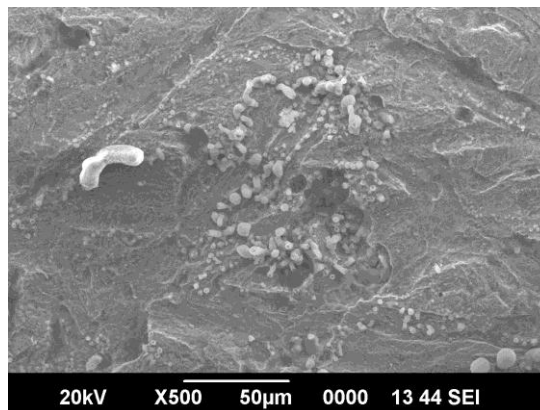


Fig: 14. SEM image of mild steel after immersion in 1M HCl with inhibitor PQML 300ppm

3.7/ Fourier transform infrared spectroscopic studies (FTIR)

FT-IR analysis was conducted to identify the functional groups present in the extracts and the corrosion product and to confirm the inhibition taking place due to the interaction between the extract and metal. Tables 9, 10,11 & 12 show various bonds present in the corrosion product and extract. When mild steel was immersed in the extract to form the corrosion product, there occurred a shift in the spectra of the extract, showing an interaction between mild steel and extract resulting inhibition. Spectra of the corrosion product show some functional groups missing, which might have occurred due to adsorption of the inhibitor on the mild steel surface.

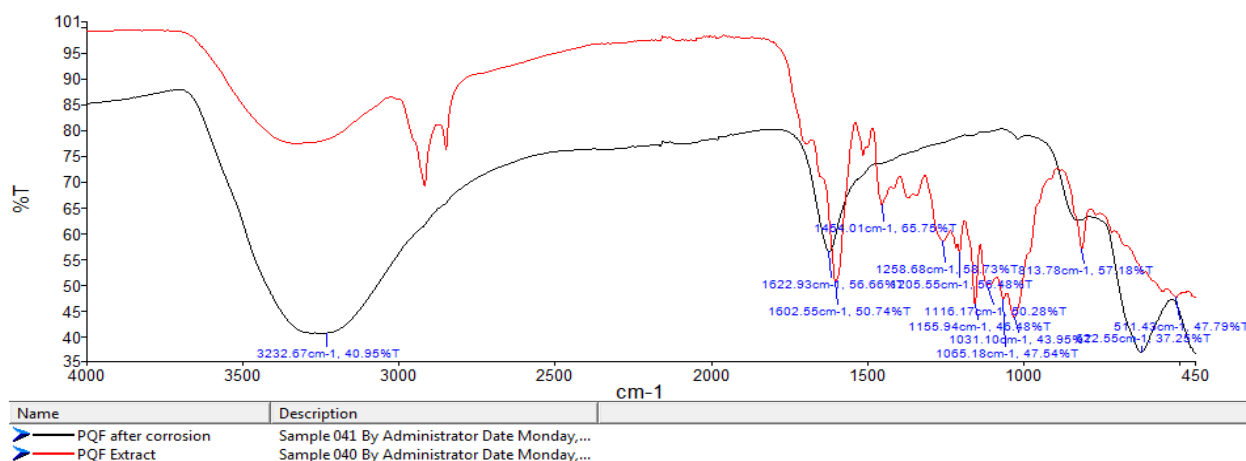


Fig :15. FTIR spectra of crude plant extract and corrosion product – PQMF

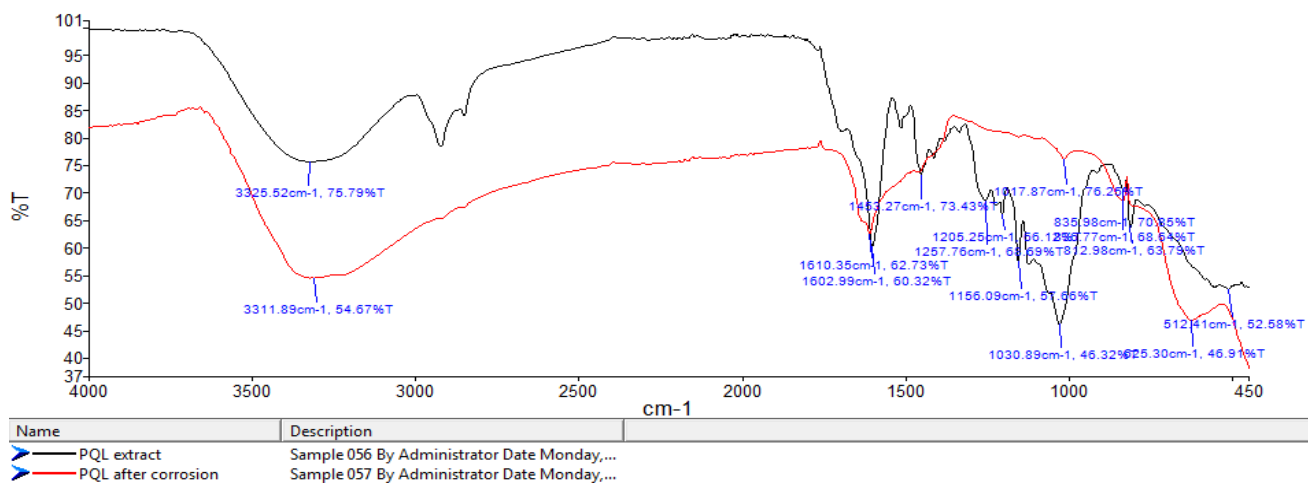


Fig :16. FTIR spectra of crude plant extract and corrosion product – PQML

Table 9. IR spectra of PQML extract

Wave number (cm ⁻¹)	Assignment/ vibration mode
3325	O-H stretching
2937	C-H stretching
1602.99	C=C
1453.26	C-H bending
1257.76	C-N stretching
1156.09	C-O stretching
812.98	N – H bending

Table 10. IR spectra of corrosion product PQML

Wave number (cm ⁻¹)	Assignment/ vibration mode
3311.89	O- H stretching
1610.35	C=C vibration
1017.87	-C-O stretching
836.77	N-H bending

Table 11. IR spectra of PQMF extract

Wave number (cm ⁻¹)	Assignment/ vibration mode
3313	O-H stretching
2920.40	C-H stretching
1602.55	C=C
1454.01	C-H bending
1258.68	C-N stretching
1155.94	C-O stretching

Table 12. IR spectra of corrosion product PQMF

Wave number (cm ⁻¹)	Assignment/ vibration mode
3232.67	O- H stretching
1622.93	C=C vibration
622.55	Fe ₂ O ₃

Conclusion

Experimental studies proved that PQML and PQMF are very effective inhibitors for mild steel corrosion in 1 M HCl and PQMF are more effective than PQML and the inhibition efficiency increased with increase in extract concentration. Gravimetric technique and EIS studies strongly suggest the formation of protective barrier by PQML and PQMF on mild steel surface which is supported by SEM studies and FTIR. Polarisation studies revealed that the extract inhibited corrosion process by means of a mixed inhibition mechanism. Adsorption of PQML and PQMF was further confirmed by experimental data fitting to Langmuir adsorption isotherm. The results obtained using electrochemical polarisation and EIS techniques are in good agreement. DFT – based quantum chemical computations of parameters associated with the electronic structures of major components EDC and GVE confirmed the inhibiting potential of PQML and PQMF.

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Conflict of interest

The authors hereby declare that there are no known conflicts of interest associated with this publication. We hereby confirm that the manuscript has been read and approved by all the authors and the order of authors listed in the manuscript has been approved by all.

References

1. P.A. Schweitzer, *Fundamentals of corrosion. Mechanism, causes and preventive methods*. CRC Press, UK. ISBN 9781420067705 (2012) , 403 pp.
2. E. Mc. Cafferty, *Introduction to Corrosion Science*. Springer Science + Business Media, LLC, New York. ISBN 978-1-4419-0455-3, (2010). [doi:10.1007/978-1-4419-0455-3](https://doi.org/10.1007/978-1-4419-0455-3)
3. H. Kumar, V. Yadav, Corrosion characteristics of mild steel under different atmospheric conditions by vapour phase corrosion inhibitors. *Am. J. Mater. Sci. Eng.* 1 (2013) 34 -39. [DOI: 10.12691/ajmse-1-3-1](https://doi.org/10.12691/ajmse-1-3-1)
4. M. Finsgar, J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review. *Corros. Sci.* 86 (2014) 17 – 41. [http:// dx.doi.org/10.1016/j.corsci.2014.04.044](http://dx.doi.org/10.1016/j.corsci.2014.04.044)
5. P. Rajeev, A.O. Surendranathan, C.S.N. Murthy, Corrosion mitigation of the oilwell steels using organic inhibitors – a review. *J. Mater. Environ. Sci.* 3 (5) (2012) 856 – 869.
6. W. Graeme , Corrosion protection of metals in marine environment. *J. Metal Corrosion Protection*, Chemistry Department, University of Auckland. (2010).
7. K.K Anupama , J. Abraham , Electroanalytical studies on the corrosion inhibition behaviour of guava (*Psidium guajava*) leaves extract on mild steel in hydrochloric acid. *Res. Chem. Intermed.* 39 (2013) : 4067 – 4080. <https://doi.org/10.1007/s11164-012-0923-0>
8. R. Singh, Corrosion control and monitoring. In *Corrosion control for offshore structures: Cathodic protection and high efficiency coating*. (2014) pp. 41 - 44.
9. Al –Otaibi M S., Al- Mayouf A M ., Khan M., Mousa A A ., Al – Mazroa S A., Alkhathlan H Z. 2014. Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. *Arabian J. Chem.* <https://doi.org/10.1016/j.arabjc.2012.01.015>
10. M.M. Solomon, S.A. Umoren , Enhanced corrosion inhibition effect of polypropylene glycol in the presence of iodide ions at mild steel / sulphuric acid interface. *J. Environ. Chem. Eng.* 3 (3) (2015) 1812-1826. <https://doi.org/10.1016/j.jece.2015.05.018>
11. A. Dutta, S.K. Saha, P. Banerjee, D. Sukul, Correlating electronic structure with corrosion inhibition potentiality of some bis - benzimidazole derivatives for mild steel in hydrochloric acid : combined experimental and theoretical studies. *Corros. Sci.* 98 (2015) 541 -550. <https://doi.org/10.1016/j.corsci.2015.05.065>
12. A. Popova , M. Christov, A. Vasilev, Mono – and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part III : influence of temperature on the inhibition process, *Corros. Sci.* 94 (2015) 70 -78. <https://doi.org/10.1016/j.corsci.2015.01.039>
13. M. Yadav, R.R. Sinha, S. Kumar, I. Bahadur, E.E. Ebenso, Synthesis and application of new acetohydrazide derivatives as a corrosion inhibitor of mild steel in acidic medium: insight from electrochemical and theoretical studies, *J. Mol. Liq.* 208 (2015) 322 – 332. <https://doi.org/10.1016/j.molliq.2015.05.005>
14. P. Singh, E.E. Ebenso, L.O. Olasunkanmi, I.B. Obot, M.A. Quraishi, Electrochemical, theoretical and surface morphological studies of corrosion inhibition effect of green naphthyridine derivatives on mild steel in hydrochloric acid. *J. Phys. Chem C* 120 (2016) 3408 -3419. [DOI: 10.1021/acs.jpcc.5b11901](https://doi.org/10.1021/acs.jpcc.5b11901)
15. M. Yadav, L. Gope , N. Kumari, P. Yadav , Corrosion inhibition performance of pyranopyrazole derivatives for mild steel in HCl solution: gravimetric, electrochemical and DFT studies, *J. Mol. Liq.* 216 (2016) 78 -86. <https://doi.org/10.1016/j.molliq.2015.12.106>
16. E. Baran, A. Cakir, B. Yazici, Inhibitory effect of *Gentiana olivieri* extracts on the corrosion of mild steel in 0.5 M HCl: Electrochemical and phytochemical evaluation. *Arabian J. Chem.* (in press) , [https:// dx. doi. org /10/ 1016/ j.arabjc.2016. 06.008.](https://dx.doi.org/10.1016/j.arabjc.2016.06.008)
17. K.K. Anupama , K. Ramya , K.M. Shainy , A. Joseph, Adsorption and electrochemical studies of *Pimenta dioica* leaf extracts as corrosion inhibitor for mild steel in hydrochloric acid. *Mater. Chem. Phys.* 167 (2015) : 28 – 41. <http://dx.doi.org/10.1016/j.matchemphys.2015.09.013>

18. K.K. Anupama, K. Ramya, A. Joseph, Electrochemical and computational aspects of surface interaction and corrosion inhibition of mild steel in hydrochloric acid by *Phyllanthus amarus* leaf extract (PAE). *J. Mol. Liq.* 216 (2016) : 146 – 155. <http://dx.doi.org/10.1016/j.molliq.2016.01.019>
19. K.K. Anupama , K.M. Shainy , A. Joseph, Excellent anticorrosion behaviour of *Ruta graveolens* extract (RGE) for mild steel in hydrochloric acid : Electroanalytical studies on the effect of time, temperature and inhibitor concentration. *J. Bio. Tribo. Corros.* 2 (2016) 2. <http://dx.doi.org/10.1007/s40735-016-0032-5>
20. A.S.Fouda ,A.S.Abousalem, G.Y.El- Ewady, Mitigation of corrosion of carbon steel in acidic solutions using an aqueous extract of *Tilia cordata* as green corrosion inhibitor. *Int. J. Ind.Chem.* 8 (2017) : 61 -73. <http://dx.doi.org/10.1007/s40090-016-0102-z>
21. C. Verma, M.A. Quarishi, Adsorption behaviour of 8,9 –bis (4 (dimethyl amino) phenyl) benzo (4,5) imidazo(1,2 –a) pyridine-6,7 – dicyanonitrile on mild steel surface in 1 M HCl. *J. Assoc. Arab Univ. Basic Appl. Sci.* 22 (2017) 56 – 61. <https://doi.org/10.1016/j.jaubas.2016.01.003>
22. G.R. Bhatti , M. Ingrouille. Systematics of *Pogostemon* (Labiatae). *Bull. Nat. Hist. Mus. Bot. Ser.*, 27 (1997) 77-147.
23. R.V. Lansdown, *Pogostemon quadrifolius*. The IUCN Red List of Threatened Species, Version 2014.3. (2011) ISBN: 9781592599691, <http://www.iucnredlist.org/details/classify/199696/0>
24. Jisha M., Hukuman N H Z, Leena P, Corrosion inhibition and adsorption studies by *Pogostemon quadrifolius* methanolic stem extract (PQMSE) on mild steel in 1 M HCl. *Int. J. Adv. Chem.* 6 (2) (2018) 157-162. <http://dx.doi.org/10.14419/ijac.v6i2.13702>
25. S. Cheriyaundath , R. Raghavan , A. Banerji, K.D. Klika, C. Ulrich , R.W.Owen, J. Madassery, Bioassay – guided isolation and evaluation of antiproliferative effects of (Z) - Ethylidene-4,6-dimethoxycoumaran-3-one from *Pogostemon quadrifolius* (Benth.). *Asian Pac J Cancer Prev.*, 18 (7) (2017) 1783-1790. [DOI:10.22034/APJCP.2017.18.7.1783](https://doi.org/10.22034/APJCP.2017.18.7.1783)
26. M. Jisha, N.H.Z. Hukuman, P. Leena , GC- MS analysis of leaves and flowers of *Pogostemon quadrifolius* (Benth.) F. Muell. (Lamiaceae). *World J. Pharm. Res.* 5 (12) (2016) 667-681. [doi:10.20959/wjpr201612-7402](https://doi.org/10.20959/wjpr201612-7402)
27. R.R. Anand , R.M. Hurd , N.Hackerman , Adsorption of monomeric and polymeric amino corrosion inhibitors on steel. *J. Electrochem. Soc.* 112 (1965) 138- 144. <http://dx.doi.org/10.1149/1.2423482>
28. R.A. Prabhu, A.V. Shanbag , V.T. Venkatesha, Influence of tramadol[2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)cyclohexanolhydrate] on corrosion inhibition of mildsteel in acidic media, *J. Appl. Electrochem.* 37 (2007) 491 -497.
29. R. Nabah H. Lgaz, H. Zarrok, M. Larouj, F. Benhiba, K. Ourrak, M. Cherkaoui, A. Zarrouk, R. Tourir, H. Oudda, Anti-corrosion properties of niaouli essential oil for tinsplate in 3 % NaCl medium, *J. Mater. Environ. Sci.* 8 (10) (2017) 3730-3739.
30. A. Bouoidina A., El-Hajjaji F., Chaouch M., Abdellaoui A., Elmsellem H., Rais Z., Filali Baba M., Lahkimi A., Hammouti B. and Taleb M., *Der Pharma Chemica*, 8(13) (2016)149-157
31. L. Bammou, M. Mihit, R. Salghi, L. Bazzi, A. Bouyanzer, S.S. Al-Deyab, B. Hammouti, Inhibition Effect of Natural Artemisia Oils Towards Tinsplate Corrosion in HCl solution: Chemical Characterization and Electrochemical Study, *Int. J. Electrochem. Sci.*, 6 N°5 (2011) 1454-1467.
32. M.K. Bagga, R. Gadi, O.S. Yadav, R. Kumar, R. Chopra, G. Singh, Investigation of phytochemical components and corrosion inhibition property of *Ficus racemosa* stem extract on mild steel in H₂SO₄ medium, *J. Environ. Chem. Eng.* 4 (2016) 4699. [10.1016/j.jece.2016.10.022](https://doi.org/10.1016/j.jece.2016.10.022)
33. Dahmani M., Et-Touhami A., Al-Deyab S.S., Hammouti B., Bouyanzer A., Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine, *Int. J. Electrochem. Sci.*, 5 (2010) 1060- 1069.
34. D. Bouknana, B. Hammouti, M. Messali, A. Aouniti, M. Sbaa, Phenolic and non-Phenolic Fractions of the Olive Oil Mill Wastewaters as Corrosion Inhibitor for Steel in HCl medium, *Port. Electrochim. Acta*, 32 (2014) 1-19. [10.4152/pea.201401001](https://doi.org/10.4152/pea.201401001)

35. A.I. Ali, H.E. Megahed, M.A. El-Etre, M.N. Ismail, Zinc corrosion in HCl in the presence of aqueous extract of *Achillea fragrantissima*, *J. Mater. Environ. Sci.* 5 (2014) 923-930
36. Cinnamon essential oil as a novel eco-friendly corrosion inhibitor of copper in 0.5 M Sulfuric Acid medium, K. Dahmani, M. Galai, M. Cherkaoui, A. El hasnaoui, A. El Hessni, *J. Mater. Environ. Sci.*, 8 (5) (2017) 1676-1685
37. K. M. Emran, N. M. Ahmed, B. A. Torjoman, A. A. Al-Ahmadi, S. N. Sheekh, Cantaloupe Extracts as Eco Friendly Corrosion Inhibitors for Aluminum in acidic and alkaline solutions, *J. Mater. Environ. Sci.* 5 (6) (2014) 1940-1950
38. G. Gece, The use of quantum chemical methods in corrosion inhibitor studies. *Corros. Sci.* 50 (11) (2008) 2981–2992. <https://doi.org/10.1016/j.corsci.2008.08.043>
39. P R. Ammal, R P. Anupama, A Joseph, in press. Comparative studies on the electrochemical and physicochemical behaviour of three different benzimidazole motifs as corrosion inhibitor for mild steel in hydrochloric acid. *Egypt. J. Petrol.* 27 (2018) 1067-1076, <https://doi.org/10.1016/j.ejpe.2018.03.006>
40. G. Karthik, M. Sundaravadivelu, Studies on the inhibition of mild steel corrosion in hydrochloric acid solution by atenolol drug, *Egypt. J. Petrol.* 25 (2016) 183 -191. <http://dx.doi.org/10.1016/j.ejpe.2015.04.003>
41. J. Sam, K. Mathew, A. Joseph, Adsorption and inhibition effect of methyl carbamate on copper metal in 1N HNO₃: an experimental and theoretical study. *RSC Adv.* 3 (2013) 8929–8938. doi:[10.1039/C3RA40922H](https://doi.org/10.1039/C3RA40922H)
42. K. Ramya, A. Joseph, Synergistic effects and hydrogen bonded interaction of alkyl benzimidazoles and thiourea pair on mild steel in hydrochloric acid. *J. Taiwan Inst. Chem. Eng.* 52 (2015) 127 -139. <http://dx.doi.org/10.1016/j.jtice.2015.01.027>
43. I. Lukowits, E. Kalman, F. Zucchi, Corrosion inhibitors - correlation between electronic structure and efficiency. *Corrosion* 57 (1) (2001) 3 -8. <https://doi.org/10.5006/1.3290328>

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