



Corrosion inhibition and adsorption studies by Pogostemon- quadrifolius methanolic stem extract (PQMSE) on mild steel in 1M HCL

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Abstract

Pogostemon quadrifolius methanolic stem extract (PQMSE) has been investigated as non toxic green corrosion inhibitor for mild steel in 1 M HCl. Corrosion rates were evaluated at 303 K, 313 K and 323 K by weight loss method at varying inhibitor concentrations. Using electrochemical impedance spectroscopy (EIS) and polarisation techniques, corrosion studies were done at 303 K in various inhibitor concentrations. Adsorption studies were also conducted to study the mechanism of corrosion inhibition. Scanning electron microscopy (SEM) and Fourier – transform infrared (FT-IR) spectroscopy were used to study the surface morphology of mild steel. Electrochemical studies reveal that PQMSE exhibit excellent corrosion inhibition efficiency and it function as a mixed type of inhibitor at 303 K. The surface interaction of PQMSE on mild steel in 1 M HCl was obeying Langmuir adsorption isotherm at all studied temperatures.

Keywords: Pogostemon quadrifolius; Stem; Corrosion Inhibitor; Weight Loss; Electrochemical Studies; Adsorption.

1. Introduction

Corrosion of metals has always been an interesting topic among corrosion scientists and engineers. Mild steel hydrochloric acid system and the behaviour of corrosion inhibitors in such systems have gained great importance in the past decades. Inhibitors are used in acid solutions during acid pickling, cleaning in industries, oil - wellacidization, for removal of rust, corrosion products and scale etc (Mourya et al., 2014; Krishnegowda et al., 2013; Ji et al., 2015; Raja et al., 2013). Various organic and inorganic compounds have been investigated as efficient and effective corrosion inhibitors (Finsgar and Jackson, 2014). Many inorganic inhibitors, especially those containing chromate, phosphate and other heavy metals are banned due to their toxicity and the threat caused to aquatic ecosystems (Roy et al., 2014). Toxicity and high cost of manufacturing interrupted the extensive use of synthetic organic corrosion inhibitors. This resulted in the exploration of cheap biodegradable ecofriendly green corrosion inhibitors. Natural plant extracts are analogous to the synthetic organic inhibitors and are proven efficient as their synthetic counterparts (Chigondo and Chigondo, 2016).

Due to natural origin, non toxic nature and negligible negative impacts on aquatic ecosystems, drugs were considered as ideal corrosion inhibitors like many plant extracts until recent years (Raja and Sethuraman, 2008; Newman et al., 2003; Newman and Cragg, 2007; Harvey, 2008; Struck et al., 2008). But not all drugs are readily biodegradable and their transformation products may be equally or even more hazardous to the environment and so more studies are needed before any drugs are concluded as ecofriendly corrosion inhibitor. The possible negative impacts of pharmaceutical contaminants are still under investigation and so the suitability of a drug as a green corrosion inhibitor should be as-

sessed every time (Gece, 2011). Hence natural plants extracts form a better green corrosion inhibitor. Pogostemon quadrifolius (Benth.) of Lamiaceae is a common ethnobotanically important medicinal shrub in India, Bangladesh and Myanmar, which is used as a folk medicine against chicken pox worms and also as a blood purifier (Bhatti and Ingrouille, 1997; Lansdown, 2011; Biswas et al., 2010; Padal and Chandrasekhar, 2013; Padal et al., 2013; Padal and Raju, 2013; Raju et al., 2014). The plant is well known for its antioxidant, mosquito larvicidal, antiproliferative and antimicrobial activities (Cheriyamundath et al., 2015; 2015a, 2015 b; Klika et al., 2014; Thoppil et al., 2003; Trivedi, 2006; Pushpalatha, 2015; Jisha et al., 2016; Jisha and Hukuman, 2017). The chemical constituents of P. quadrifolius, both qualitative and quantitative, have also been well studied (Jisha et al., 2016 a, Jisha et al., 2017a, b). The corrosion inhibition activity of P. quadrifolius has not been studied so far. In the present study, the corrosion inhibition property of the methanolic extract of the stem of P. quadrifolius (PQMSE) for mild steel in 1 M HCl has been reported. Weight loss method, electrochemical impedance spectroscopy, potentiodynamic polarization technique, FT –IR and SEM were employed.

2. Materials and methods

2.1. Inhibitor preparation

The fresh stems of P. quadrifolius were collected from Karimbam, Kannur, Kerala and authenticated from Department of Botany, University of Calicut. The collected stems were washed, shade dried for 3 weeks and made into fine powder using a mixer grinder and the powder was kept in small airtight bottles with proper labelling. Powdered stems were extracted using methanol in Soxhlet

apparatus. The extracts were then filtered and evaporated to dry, which were used as the corrosion inhibitor.

2.2. Mild steel specimen and medium

Mild steel of size $2 \times 1.9 \text{ cm}^2$ having a composition of C (0.2%), Mn (1%), S (0.2 %) P (0.3%) and Fe (98.75%) were used for weight loss studies. The steel specimens were rubbed well with different grades of emery paper and degreased with acetone prior to the study. They were washed well, dried and used for weight loss studies.

Test solution of 1 M HCl was prepared by diluting analytical grade HCl (Merck) with double distilled water.

2.3. Weight loss method

The corrosion inhibition activities of the extracts for mild steel in 1 M HCl was determined by weight loss measurements at 303 K, 313 K and 323 K. Mild steel specimens which were weighed previously were immersed in 50 ml 1M HCl solution containing different concentrations of inhibitor (100 ppm, 150ppm, 200 ppm, 250 ppm and 300 ppm) for 6 hours. Steel specimens immersed in 1M HCl without inhibitor was considered as blank. The immersed steel specimens were taken out after 6 hours, washed with water, cleaned with acetone, dried and weight determination was done. The corrosion rate and inhibition efficiencies were determined following standard procedures (Bribri et al., 2013) with the following equations.

$$\text{Corrosion rate (C}_R\text{)} = (W_b - W_a) / A * t \quad (1)$$

$$\text{Inhibition efficiency (IE \%)} = [(W_1 - W_2) / W_1] * 100 \quad (2)$$

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, W_1 the weight loss without inhibitor and W_2 the weight loss with inhibitor.

2.4. Electrochemical measurements

The electrochemical impedance and polarisation studies were conducted using Gill AC computer controlled work station (Model 1475: ACM, UK). The experiments were conducted at 303 K temperature using a conventional three electrode cell assembly. Mild steel specimen with exposed surface area 1 cm^2 in the investigation was the working electrode, saturated calomel and platinum foil electrodes were the reference and auxiliary electrodes. Meas-

urements were taken without and with different concentrations of stem extract of *P. quadrifolius* as corrosion inhibitor. In order to attain stability, mild steel specimens were immersed in the solutions for 1 hour before measurements.

Electrochemical impedance spectroscopy (EIS) was carried out applying a sinusoidal voltage of amplitude 10mV with a frequency range 10 kHz to 0.1 Hz. Nyquist plots represent the impedance measurements. Inhibition efficiencies were calculated using the equation

$$\text{IE (\%)} = \frac{R_{ct}^* - R_{ct}}{R_{ct}^*} \times 100 \quad (3)$$

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

Tafel plots represent potentiodynamic polarization measurements (+250 to -250 mV potential range with scan rate 60mV/min). By extrapolating the linear segments of anodic and cathodic polarization curves to corrosion potential (E_{corr}) at different inhibitor concentrations, corrosion current density (i_{corr}) was obtained. The corrosion inhibition efficiency was evaluated from the measured i_{corr} values as,

$$\text{IE (\%)} = \frac{i_{corr} - i_{corr}^*}{i_{corr}} \times 100 \quad (4)$$

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

3. Results and discussion

3.1. Weight loss method

Table 1 provides the weight loss measurement results conducted at 303 K, 313 K and 323K. Methanolic extract of the stem of *P. quadrifolius* show good corrosion inhibition for mild steel in 1 M HCl. It shows a high inhibition efficiency of 95.20 % at 303 K, 92.41 % at 313 K and 89.30 % at 323 K respectively at 300ppm concentration. Corrosion rates showed tremendous decrease with increase in concentration of the inhibitor and inhibition efficiency of the extract increased with concentration of inhibitor. The high inhibition efficiency of the extract at high concentration may be due to blocking of active sites against corrosion by the adsorption of inhibitor on the surface of mild steel as suggested by previous workers (Anupama et al., 2015, 2016; Fouda et al., 2017; Shukla and Ebenso, 2011).

Table 1: Corrosion parameters for mild steel in 1 M HCl by weight loss method at different temperatures in the absence and presence of inhibitor.

Temperature	Concentration of plant extract in 1M HCl (ppm)	Weight of steel before immersion	Weight of steel after immersion	Weight loss	$W_b - W_a$	Corrosion rate (CR in $\text{g/cm}^2\text{h}$)	Inhibition Efficiency (IE %)
303 K	Blank	3.745	0.319	3.426		0.939	
	100	3.671	2.8228	0.8482	2.5778	0.233	75.24
	150	3.711	3.0364	0.6746	2.7514	0.185	80.31
	200	3.711	3.2067	0.5043	2.9217	0.138	85.28
	250	3.73	3.408	0.3220	3.104	0.088	90.60
	300	3.681	3.5166	0.1644	3.2616	0.045	95.20
313 K	Blank	3.745	0.319	3.426		0.939	
	100	3.67	2.7502	0.9198	2.5062	0.2521	73.15
	150	3.681	2.9417	0.7393	2.6867	0.2026	78.42
	200	3.73	3.148	0.5820	2.844	0.1595	83.01
	250	3.745	3.3374	0.4076	3.0184	0.112	88.10
	300	3.712	3.452	0.260	3.166	0.0712	92.41
323 K	Blank	3.745	0.319	3.426		0.939	
	100	3.71	2.689	1.021	2.405	0.2798	70.21
	150	3.681	2.8632	0.8178	2.608	0.2241	76.13
	200	3.731	3.0629	0.6681	2.7579	0.1831	80.50
	250	3.741	3.2665	0.4745	2.9515	0.1300	86.15
	300	3.689	3.3224	0.3666	3.0594	0.1004	89.30

3.2. Electrochemical studies

3.2.1. Electrochemical impedance spectroscopic studies (EIS)

EIS data for mild steel in 1 M HCl was determined without and with the presence of inhibitor at concentrations 100 ppm, 200 ppm and 300ppm at 303K. The results obtained are represented as Nyquist plots in Figure 1. Charge transfer resistance (R_{ct}), provided as the diameter of the semicircle, increases with increasing inhibitor concentration. Nyquist plots obtained are not perfect semicircles. This may be due to surface inhomogeneity, roughness or impurities etc (Anupama et al., 2015; Prabhu et al., 2007; Anand et al., 1965). The various impedance data such as charge transfer resistance (R_{ct}), corrosion current density (I_{corr}) and inhibition efficiency (IE) as obtained from Nyquist plots are provided in table 2. Table 2 clearly shows that charge transfer resistance increased with increase in concentration of PQ stem extracts. This may be due to the formation of protective film on metal solution interface due to the adsorption of the inhibitor on the most active adsorption sites (Anupama et al., 2015).

Fig. 1:

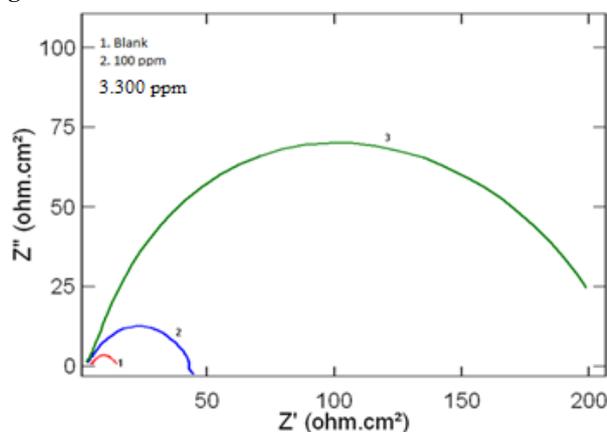


Fig. 2:

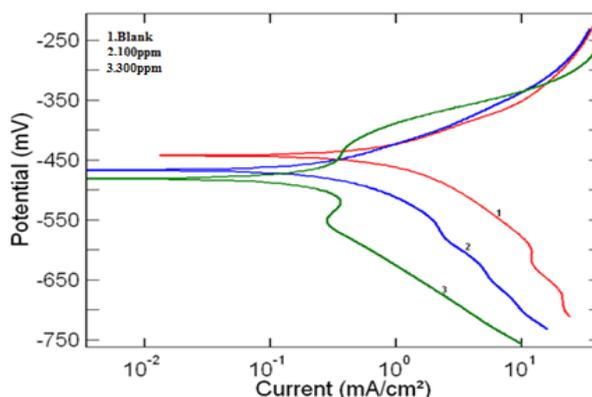


Table 3: Polarisation data for mild steel in 1 M HCl without and with methanolic extracts of stem of PQ

Sample	Concentration of inhibitor (ppm)	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (mA cm ²)	C_r (mm/yr)	IE %
Blank		-443	117	173	1.662	19.262	
PQ stem extract	100	-467	97.00	127	0.471	5.434	71.60
	300	-482	71	146	0.126	1.458	92.40

3.3. Adsorption studies and thermodynamic parameters

Metal – inhibitor interaction is due to adsorption of an organic molecule on the metal surface, which is a replacement reaction and it can be well studied by analysing the adsorption process using adsorption isotherms (Li, 2011). The surface interaction of PQMSE on mild steel in 1 M HCl was obeying Langmuir adsorp-

Table 2: EIS data for mild steel in 1 M HCl without and with methanolic extract of stem of PQ

Sample	Concentration of inhibitor (ppm)	R_{ct} (Ω cm ²)	I_{corr} (mA cm ²)	C_r (mm/yr)	IE%
Blank	-----	9.256	2.818	32.67	-----
PQ stem extract	100	41.92	0.623	7.212	77.91
	200	55.42	0.471	5.456	83.29
	300	194.00	0.135	1.558	95.21

3.2.2. Potentiodynamic polarisation studies

The potentiodynamic polarization curves for mild steel in 1 M HCl without and with PQMSE of concentration 100 ppm and 300 ppm are shown in Figure 2. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate (C_r), cathodic Tafel constant (β_c) and anodic Tafel constant (β_a) were determined from the polarisation curves and are provided in table 3. The inhibition efficiency (IE%) of the PQMSE were calculated using equation 4 and provided in the table 3. It can be observed from the polarization results that the I_{corr} values decrease considerably in the presence of PQMSE from 100 ppm to 300 ppm. Addition of PQMSE slightly modifies the Tafel slopes. In the presence of 100 ppm and 300 ppm PQMSE in 1 M HCl, no definite trend was observed in the shift of E_{corr} values. Thus it may be concluded that PQMSE exhibit cathodic and anodic inhibition showing relatively mixed type of inhibition behaviour in 1 M HCl. The trend in inhibition efficiency obtained in EIS studies is in agreement with potentiodynamic polarization studies.

tion isotherm at all temperatures (303K, 313K and 323K). Langmuir adsorption isotherm is described 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. Figure 3 represent the Langmuir adsorption isotherm which is found to be linear. In the present study the value of correlation

coefficient (R^2) was obtained close to unity for Langmuir adsorption isotherm.

The free energy of adsorption (ΔG_{ads}) can be calculated using the equation

$$\Delta G_{ads} = -RT \ln(1000 \cdot K_{ads}) \quad (6)$$

where K_{ads} is the adsorption equilibrium constant. From table 4, it can be identified that ΔG_{ads} values are negative, which is an indication of the spontaneity of adsorption and it shows the stability of adsorbed layer on mild steel surface (Keles et al., 2008; Fouda et al., 2009). It is said that the values of ΔG_{ads} obtained around -20 kJ/mol or lower indicate physisorption whereas the values around -40 kJ/mol indicate chemisorption (Ahmad et al., 2010; Ozcan et al., 2008; Noor and Al- Moubaraki, 2008). Regarding an organic molecule, the adsorption phenomenon cannot be considered as purely physical or chemical adsorption (Solmaz, 2010; Doner et al., 2011). In the present investigation the value of ΔG_{ads} was between -20 kJmol $^{-1}$ and -40 kJmol $^{-1}$. Hence the adsorption of inhibitor on to the mild steel surface may involve both physisorption and chemisorption (Mohan et al., 2016).

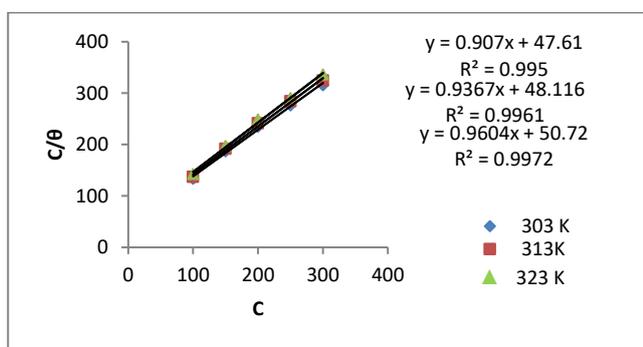


Fig. 3: Langmuir adsorption isotherm at different temperatures for mild steel in 1M HCl with different concentrations of methanol stem extracts of *Pogostemon quadrifolius* (PQMSE).

Table 4: Thermodynamic parameters calculated for the adsorption of PQMSE as inhibitor on mild steel surface in 1M HCl at different temperatures.

	Temperature (K)	K_{ads} (L.g $^{-1}$)	ΔG_{ads} (KJmol $^{-1}$)
PQM stem extract	303	21.00	25.07
	313	20.28	26.81
	323	19.72	26.56

3.4. Scanning electron microscopy

Scanning electron microscopic studies were conducted to study the surface morphology of the metal prior to and after immersion in 1 M HCl with and without the PQM stem extract (300 ppm). The results obtained are presented in Fig. 4, 5, and 6. Mild steel immersed in 1M HCl in the absence of PQMSE (Fig 5) reveal clear pits and cavities indicating severe damage by the acidic media. But such corrosion pits and cavities were absent on mild steel specimen which was immersed in 1 M HCl containing PQMSE (Fig 6) and is very much similar to the mild steel specimen before immersion in acidic solution (Fig 4). Thus it proves the idea that the extract forms a protective film on the mild steel acting as a barrier preventing the corrosion activity by acidic solutions.

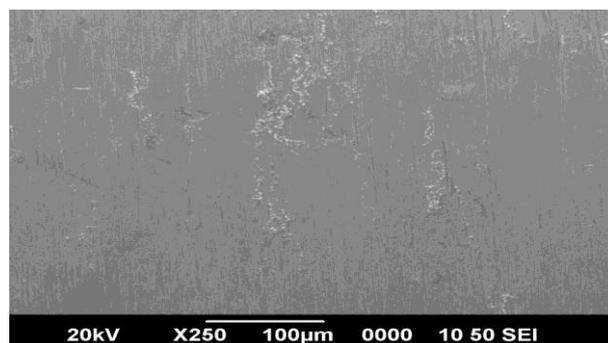


Fig. 4: SEM image of polished mild steel before immersion in test solution.

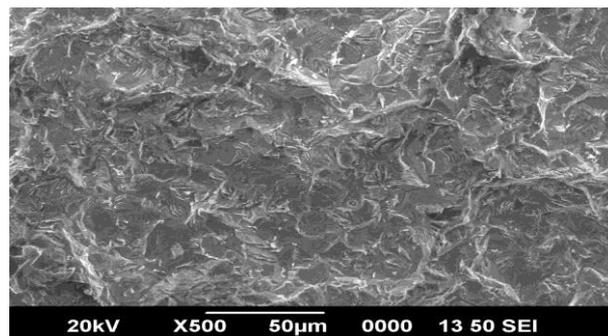


Fig. 5: SEM image of mild steel after immersion in 1M HCl without PQMSE.

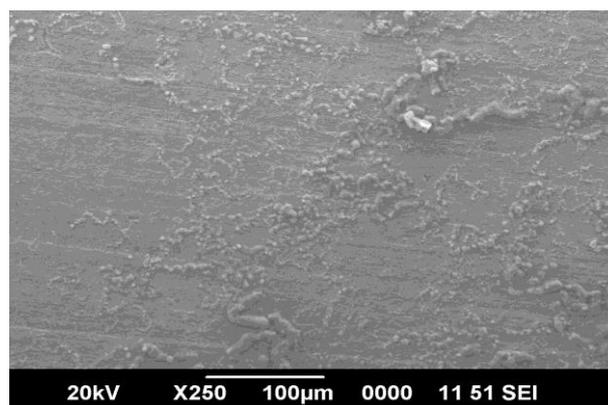


Fig. 6: SEM image of mild steel after immersion in 1M HCl with PQMSE 300ppm.

3.5. FTIR (Fourier transform infrared spectroscopy)

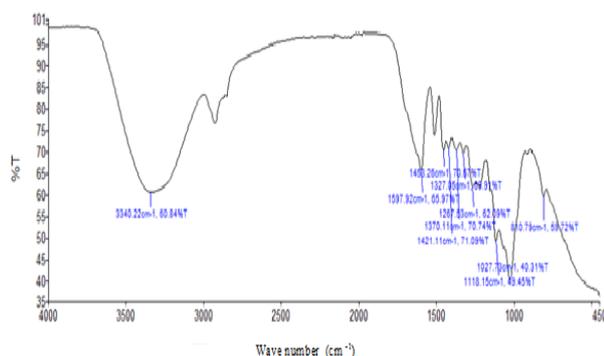
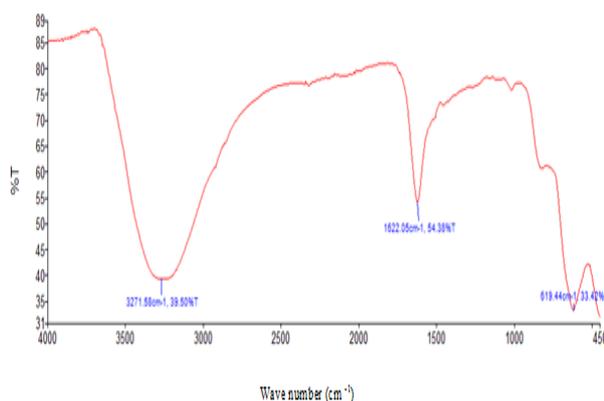
In order to identify the functional groups present in the extract FT IR analysis was carried out and that of the corrosion product was done to confirm that the inhibition takes place due to the interaction between the metal and the extract. Table 5 and 6 shows the various bonds present in the extract and the corrosion product. There is a shift in the spectra of the extract when mild steel was immersed in it to form corrosion product. This shows that there is an interaction between extract and mild steel substrate which resulted inhibition. The absorption band at 3340.22 cm $^{-1}$ indicates -OH stretching vibration. The peak at 2900 cm $^{-1}$ indicates -C-H stretching vibration. The absorption band at 1453.26 cm $^{-1}$ corresponds to C-H bending mode of CH $_2$. The absorption band $1400 - 1600$ cm $^{-1}$ indicates C-C vibration, band at 1267.53 indicates C-N stretching vibration. The absorption band in the range above 600 cm $^{-1}$ are assigned to the -C≡C-H: C-H bending vibration. The band at 1027 cm $^{-1}$ indicates C-O stretching vibration. Some functional groups were missing in the spectra of the corrosion product, suggesting that the absorption of the inhibitor on the surface of the mild steel might have occurred through the missing bands.

Table 5: IR spectra of PQMS extract

Wave number (cm ⁻¹)	Assignment/ vibration mode
3340.22	O-H stretching
2900	C-H stretching
1597.92	C=C
1453.26	C-H bending
1267.53	C-N stretching
1027	C-O stretching

Table 6: IR spectra of corrosion product

Wave number (cm ⁻¹)	Assignment/ vibration mode
3271.58	O- H stretching
1622.05	C=C vibration
619.44	C ≡ C –H , C – H bending

**Fig. 7:** FT IR spectra of crude plant extract.**Fig. 8:** FT IR spectra of the corrosion product.

4. Conclusion

- 1) Pogostemon quadrifolius methanolic stem extracts (PQMSE) act as a good corrosion inhibitor for mild steel in 1M HCl.
- 2) Weight loss studies strongly suggest the protective barrier formation by PQMSE on mild steel surface, which is supported by SEM studies and FT-IR studies.
- 3) Results obtained from EIS studies and potentiodynamic polarisation studies are in good agreement showing high inhibition efficiency by PQMSE on mild steel surface in 1 M HCl.
- 4) Polarisation technique reveals the mixed type inhibition nature of PQMSE.
- 5) The surface interaction of PQMSE on mild steel in M HCl was obeying Langmuir adsorption isotherm.

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5. Conflict of interest

The authors declare that there are no known conflicts of interest associated with this publication. We 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.

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