

Experimental and Theoretical Study of Corrosion Inhibition on Oil and Natural gas Pipeline in Acid by Marsilea Quadrifolia Extract

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Abstract: Corrosion inhibition of "Marsilea Quadrifolia" extract on oil and gas pipeline steel in 1.0N Hydrochloric acid was carried out using mass loss, potentiodynamic polarization and electrochemical impedance techniques. The inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperatures. The maximum percentage of inhibition efficiency attained is 90.44% by mass loss method. The corrosion current (I_{corr}) decreased from 3097 to 281.8 $\mu A cm^2$ with increase of inhibitor concentration studied by potentiodynamic polarization. By using impedance spectroscopy, the charge transfer resistance (R_{ct}) increased from 63.66 to 109.18 Ωcm^2 . This result is in very good agreement with the previous result. Its activation energy 62.16KJ/ mole at 1000 ppm showed that the adsorption is physical adsorption. Thermodynamic consideration revealed that adsorption is spontaneous, efficiency is maximum at 303K i.e.93.99 and found to obey Langmuir adsorption isotherm. Electrochemical studies indicated that MQL behave as a mixed type inhibitor.

Keywords: Oil and Gas pipeline steel, Marsilea Quadrifolia (MQ), 1.0N HCl, Half-life, Mass loss, Adsorption.

1. INTRODUCTION

Oil and gas pipeline being most familiar material widely employed in almost all the oil and natural gas fields in world wide. Despite the oil and gas industries facing a lot of problems of using this material which undergo dissolution in various concentrations of connate water environment presents in crude oil production. Use of green plant leaves as an inhibitor is one of the best preventive measures of metal dissolution in different aggressive environments [1-3]. Most of the well-versatile green inhibitors are organic compounds containing polar functional groups with hetero atoms viz; S, N, O and P atoms in a molecule, heterocyclic conjugated double bond with (π) electrons [4]. These kinds of compound are adsorbed onto the metallic surface of oil and gas pipeline steel and block the active corrosion surface sites. Although most of the synthetic chemicals are expensive, toxic to both human being and environment, they are non-biodegradable [5]. In order to overcome these difficulties, nowadays most of the researchers used natural products which are plenty, cheap, non-toxic and environmentally friendly as corrosion inhibitors has become a key area, and also a rich source of organic compounds [6-7]. The extract of naturally synthesized aromatic organic compounds from herbs, spices and medicinal plants, this is regarded as one of the best practical methods in preventing pipeline corrosion in oil and gas industries. Plant extracts adsorb physically or chemically on pipeline surface resulting from the interaction of their polar centers with active sites on pipeline [8-11]. Even the plant extracts are rich source of active molecules which have substantial high efficiency only for particular pipelines in certain environment and varied greatly therefore, an inhibitor may works in one well not in another

[12]. Continuous substantial studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like *Tithonia Diversifolia*, *Murraya Koenigii*, *Moringa Oleifera*, *Vernonia Amygdalina*, *Aquilaria Crassna*, *Cucurbita Maxima*, *Jatropha Curcas*, *Prunus Cerasus*, *Aloe Vera*, *Tamarind Tea leaves*, *Beet Root*, *Terminalia Bellerica*, *Oxandra Asbeckii*, *Argemone Mexicana*, *Betanin*, *Murraya Koenigii*, *Ananas Sativum*, *Artemisia Mesatlantica essential oil*, *Spirogyraalgae*, *Tragacanth gum*, *Prunus Persic*, *Lemon Grass*, *Secang heart wood extract*, *Caesalpinia sappan I*, *Dried Marjoram leaves* [13-35] have been used for inhibition of corrosion. In continuation of our work, *Marsilea Quadrifolia* extract as a potential green inhibitor on oil and gas pipeline steel in 1.0N Hydrochloric acid has been investigated with various period of immersion and temperature using mass loss and electrochemical measurements.

2. MATERIALS AND METHODS

2.1. Preparation Of Plant Extract

Marsilea Quadrifolia (MQ) were collected from Tenkasi area, washed with distilled water, dried under shadow for about 168 hours and finely powdered. About 150g of this fine powder was taken in a 500 ml round bottom flask, required quantity of ethyl alcohol was added to shield the powder completely, and left it for 48 hrs. Then the resulting paste was refluxed and the extract was collected by removing excess of alcohol and boiled with little amount of activated charcoal to remove impurities.

2.2. Sample Preparation

Rectangular specimens of area 20cm^2 ($5 \times 2 \times 2$ cm) were cut from a parent sheet of oil and gas pipeline steel. The specimens were drilled a hole at one end and numbered by punching before the use of specimen, then the electrodes were pickled with pickling solution, washed with water, rubbed with cotton cloth and dried. After pickling, the electrodes were mechanically polished with 1/0 to 5/0 emery sheets and degreased with trichloroethylene, then kept it in desiccators. These electrodes were used for this investigation

2.3. Stock Solution Of Marsilea Quadrifolia Extract

About 1g of *Marsilea quadrifolia* residue was weighed accurately dissolved in double distilled water and made up to 100 ml. From this stock solution, different concentration of 10 to 1000 ppm test solution was prepared during 1.0 N Hydrochloric acid and used throughout our present investigation.

2.4. Mass Loss Technique

In mass loss measurements, oil and gas pipeline steel specimens in triplicate were completely immersed in 100ml of the test solution in the presence and absence of MQ inhibitor. The specimens were withdrawn from the test solutions after immersion of 24 to 360 hours at room temperature and also with various temperature ranges from 303K to 333K after an hour. The mass loss of the specimens is taken as the difference in weight before and after immersion using digital balance with sensitivity of ± 1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurements, the corrosion rate was calculated using the relation.

$$\text{Corrosion Rate (mmpy)} = [87.6 \times W] / DAT \text{ -----} \rightarrow (1)$$

Where W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2) and T = time in hours.

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

$$\% \text{ IE} = [(W_1 - W_2) / W_1] \times 100 \text{ -----} \rightarrow (2)$$

$$\theta = (W_1 - W_2) / W_1 \text{ -----} \rightarrow (3)$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence of the MQL extract respectively.

2.5. Activation Energy (E_a)

Assumption of Arrhenius concept is expressed with the aid of equation (4) and its derived form (5).

$$CR = A \exp (-E_a/RT) \text{ -----} \rightarrow (4)$$

$$\log (CR2/CR1) = E_a / 2.303 R (1/T1-1/T2) \text{ ----- } \rightarrow(5)$$

Where, CR1 and CR2 are corrosion rates at temperature T1 (303K) and T2 (333K) respectively.

2.6. Heat Of Adsorption (Q_{ads})

$$Q_{ads} = 2.303 R [\log (\theta_2/1- \theta_2) - \log (\theta_1 /1- \theta_1)] \times (T_2T_1/T_2-T_1) \text{ ----- } \rightarrow(6)$$

Where, R is the gas constant, θ_1 and θ_2 are degree of surface coverage at temperatures T1 and T2 respectively.

2.7. ELECTROCHEMICAL TECHNIQUES

2.7.1. Potentiodynamic Polarization Measurement

From Tafel plot, the percentage of inhibition efficiency (IE) was determined by the following equation

$$\% IE = [(I_{Corr} - I_{Corr} (1)) / I_{Corr}] \times 100 \text{ ----- } \rightarrow(7)$$

Where $I_{Corr} (1)$ and I_{Corr} are corrosion rates in the presence and absence of inhibitors

2.7.2. Impedance spectroscopy measurement

From Nyquist plot, the percentage of inhibition efficiency (IE) was determined by the following relation.

$$\% IE = [(R_{ct} - R_{ct} (1)) / R_{ct}] \times 100 \text{ ----- } \rightarrow(8)$$

Where $R_{ct} (1)$ and R_{ct} are charge transfer resistance with and without inhibitors

3. RESULTS AND DISCUSSION

3.1. Effect of immersion time

The dissolution behavior of oil and gas pipeline steel in 1.0N Hydrochloric acid containing the presence and absence of MQ extract with various exposure times (24hrs to 360 hrs) are shown in Table-1. The observed values clearly indicate that in the presence of MQ extract, corrosion rate moderately decreased from 10.5885 to 2.3400 mmpy for 24 hrs and 0.7426 to 0.0710 mmpy after 360 hrs with increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 90.44 % inhibition efficiency is achieved after 360 hrs exposure time, suggests that the adsorption process occurs mainly due to the presence of active phytochemical constituents containing lone pair electrons in the inhibitor molecule and the metal ion from the surface of the metal.

Table-1: Corrosion parameters of oil and gas pipeline in 1.0N Hydrochloric acid containing different concentration (0 to 1000ppm) of MQ extract after 24 to 360 hours immersion time

Con.of inhibit or in ppm	Corrosion Rate in mmpy					Inhibition Efficiency (%)				
	24 Hrs	72 hrs	120 hrs	240 hrs	360 hrs	24 hrs	72 hrs	120 hrs	240 hrs	360 hrs
0	10.5885	3.627	2.2066	1.1080	0.7426	-	-	-	-	-
10	9.3132	2.9172	1.6146	0.7944	0.5015	12.04	19.57	26.83	28.30	32.47
50	7.6167	2.4297	1.3244	0.5768	0.3479	28.07	33.11	39.98	47.94	53.15
100	6.2712	1.9656	0.9524	0.3405	0.1966	40.77	45.80	56.84	69.27	73.53
500	4.0950	1.2363	0.5686	0.2469	0.1162	61.33	65.91	74.23	77.72	84.35
1000	2.3400	0.7644	0.3487	0.1439	0.0710	77.90	78.92	84.20	87.01	90.44

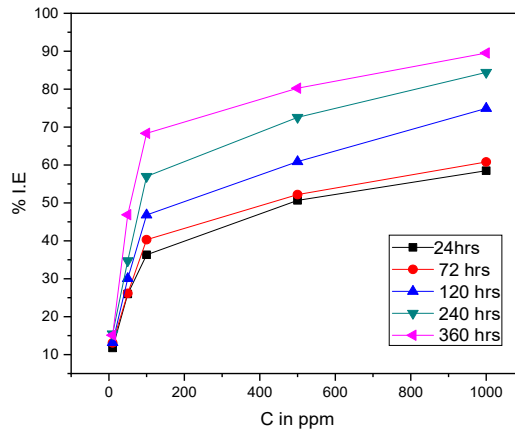


Fig-1. IE diagram of oil and gas pipeline steel in 1.0N HCl comprising different concentration of MQ with various immersion times

3.2. Kinetics and mechanism of corrosion inhibition

The logarithm of the initial weight of the oil and gas pipeline steel minus the weight of oil and gas pipeline steel in 1.0N HCl containing 500 ppm and 1000 ppm of the inhibitor concentration were plotted against time in hours and shown in Fig-2 . It reveals that the corrosion of oil and gas pipeline steel in acid medium might be of **first order kinetics**. The corrosion rate constant (K) and material half-life ($t_{1/2}$) were also calculated from the weight loss data for first order reaction using equations (9) and (10) respectively.

The rate constant of corrosion was calculated by

$$K = 2.303/T \log w_1/w_2 \text{-----} \rightarrow (9)$$

Where w_1 and w_2 are the initial and final weight of the metal (i.e.) before and after immersion. Then

$$t_{1/2} = 0.693/K \text{-----} \rightarrow (10)$$

The results obtained at various concentrations were averaged and given in table-2. The inhibitor was able to reduce the corrosion rate constant and increase the half-life and showed longer average material half-life at higher concentration. This is in agreement with the percentage corrosion inhibition efficiency data.

Table-2: Variation of Corrosion rate constant and Half-life data of oil and gas pipeline steel in 1.0 N HCl comprising different concentration of MQ

Con.in ppm	Rate constant (K)	Half-life ($t_{1/2}$) days
0	1.5629×10^{-4}	184.75
10	1.2736×10^{-4}	226.72
50	1.0336×10^{-4}	279.36
100	0.8058×10^{-4}	358.34
500	0.5120×10^{-4}	563.96
1000	0.2816×10^{-4}	1025.39

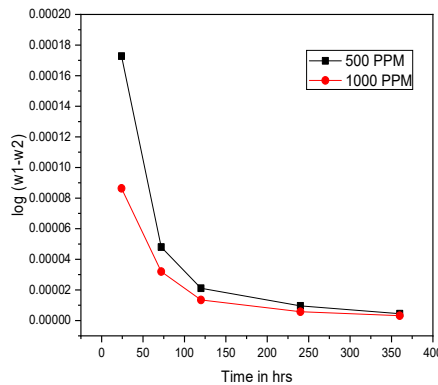


Fig-2. Plot of log (w₁-w₂) verses time for the corrosion of oil and gas pipeline steel in 1.0N HCl comprising MQ at different concentration (500 and 1000 ppm)

3.3. Effect of Temperature

Dissolution behavior of oil and gas pipeline steel in 1.0N HCl containing various concentration of MQ extract at 303 to 333K was studied and the observed values are listed in Table-3. Observed results reveal that the corrosion rate decreased with increase of inhibitor concentrations and also increased with rise in temperature from 303 to 333K. The maximum of 93.99% inhibition efficiency is achieved at 303K. However the inhibition efficiency is decreased with rise in temperature that may suggest and support the process of adsorption follows **Physisorption**.

Table-3: CR and IE data of oil and gas pipeline in 1.0N Hydrochloric acid comprising MQ at various temperatures

Con. of inhibitor (ppm)	Corrosion Rate (mmpy)			Inhibition Efficiency (%)		
	303K	313k	333K	303K	313K	333K
0	25.31	50.91	115.09	-	-	-
10	18.26	40.82	96.39	27.85	19.82	16.25
50	15.07	32.17	77.96	40.44	36.80	32.26
100	12.01	27.45	68.21	52.53	46.08	40.73
500	5.76	12.32	29.47	77.25	75.80	74.39
1000	1.52	4.25	15.44	93.99	91.65	86.58

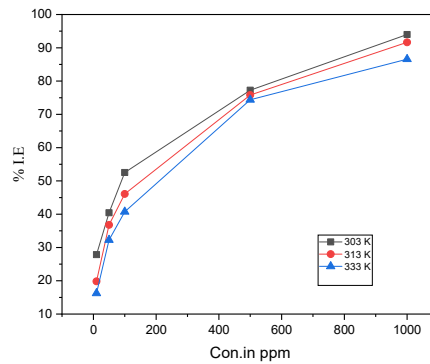


Fig-3. IE diagram of oil and gas pipeline steel in 1.0N HCl comprising MQ at various temperatures

3.4. Activation Energy

The values of corrosion rate obtained from the mass loss measurement are substituted in equation (4) and the values of activation energy (E_a) are presented in Table-4. The observed values are ranged from 40.82 to 62.16 kJ/mol(0- 1000ppm). The value of E_a obtained from the solution without inhibitor (40.82) is lower than that in the presence of inhibitor and indicated that there is a strong bond between the MQ inhibitor molecules and the mild steel surface strongly resist the dissolution of metal surface.

Table -4: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) of MQ on oil and gas pipeline steel in 1.0N HCL environment.

S.No	Con. of inhibitor(ppm)	% of I.E		E_a (KJmol ⁻¹)	Q_{ads} (KJmol ⁻¹)
		303 K	333 K		
1.	0	-	-	40.82	--
2.	10	27.85	16.25	44.63	-19.24
3.	50	40.44	32.26	44.31	-9.92
4.	100	52.53	40.73	46.67	-13.32
5.	500	77.25	74.39	43.97	-4.37
6.	1000	93.99	86.58	62.16	-24.76

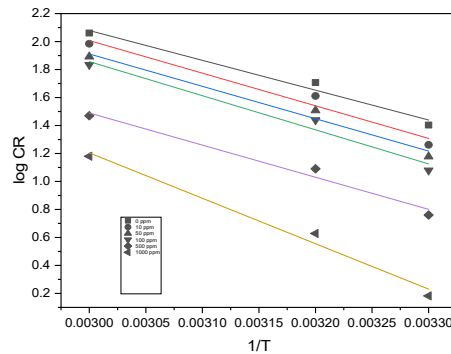


Fig-4. Arrhenius plot of oil and gas pipeline steel corrosion 1.0N HCl in the absence and presence of different concentration of MQ

3.5. Heat of Adsorption

The heat of adsorption (Q_{ads}) on oil and gas pipeline steel in 1.0N HCl containing various concentration of MQ is calculated using equation (6) and the values of Q_{ads} ranged from -19.24 to -24.76 kJ/mol (Table-4). These negative values reflected that the adsorption of MQ on oil and gas pipeline steel follows **exothermic process**

3.6. ADSORPTION STUDIES

Adsorption isotherms are very important in determining the mechanism of corrosion inhibition. The most frequently used isotherms are Langmuir, Temkin, Frumkin, Flory- Huggins, Freundlich, Bockris-Swinkles, Hill-Deboer, Parson’s and El-Awady isotherms.

3.6.1. Langmuir Isotherm

Langmuir adsorption isotherm is expressed according to equation -11,
 $\log C/\theta = \log C - \log K$ ----- $\rightarrow(11)$

Plotting $\log (C/\theta)$ against $\log C$ gave a linear relationship as shown in fig.5, and the adsorption parameters are presented in Table- 5. Average regression co-efficient value ($R^2=0.9988$) is almost close to unity ($R^2 < 1$) and obeys Langmuir adsorption isotherm, It suggested that the adsorption of MQ extract on oil and gas pipeline steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and adsorbent.

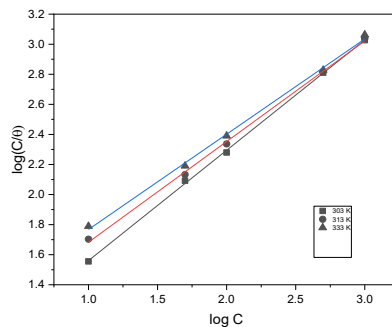


Fig -5. Langmuir isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

3.6.2. Temkin Isotherm

In Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the inhibitor concentration (c) according to equation - 12,

$$\text{Exp}(-2a\theta) = KC \text{-----} \rightarrow (12)$$

Where K= adsorption equilibrium constant and a is an attractive parameter, Rearranging and taking logarithm on both sides of equation (12) gives equation - 13

$$\theta = (-2.303\log k/2a) - (2.303\log C/2a) \text{-----} \rightarrow (13)$$

The surface coverage (θ) against $\log C$ was plotted and presented in fig-6. . Adsorption parameters obtained from Temkin adsorption isotherm are recorded in Table-5. The average regression co-efficient (R^2) is 0.9718 far away from unity. However values of attractive parameter (a) are positive, indicating that there is no interaction between the adjacent molecules in the adsorbed layer.

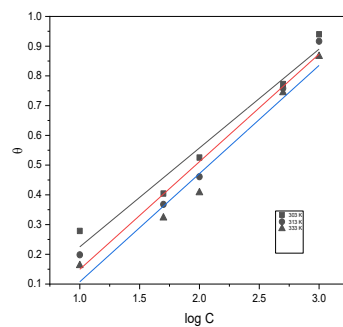


Fig-6. Temkin isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

3.6.3. Flory-Huggins Isotherm

Flory-Huggins adsorption isotherm can be expressed according to equation (14)

$$\log(\theta/C) = \log K + x\log(1-\theta) \text{-----} \rightarrow (14)$$

The plot of $\log(\theta/C)$ against $\log(1-\theta)$ is shown in fig-7, and obtained data are given in table-5. The average regression co-efficient (R^2) 0.8562 is very far away from the unity. The values of the size parameter(x) are positive which indicates that the adsorbed species of ethanol extract of MQ is bulky, since it could displace number of water molecules and occupying adsorption sites on the surface of oil and gas pipeline steel

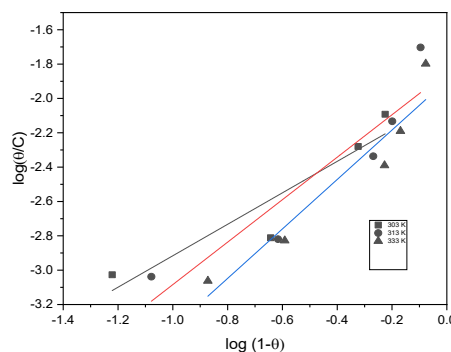


Fig-7. Florry-Huggins isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

3.6.4. Frumkin Isotherm

Frumkin adsorption isotherm is given by equation (15)

$$\log \{ [C]^* (\theta/1-\theta) \} = 2.303 \log K + 2\alpha\theta \quad \rightarrow(15)$$

where k is the adsorption–desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer. The plot of $\log \{ [C]^* (\theta/1-\theta) \}$ versus θ as presented were linear which shows that the applicability of Frumkin isotherm. The values for Frumkin adsorption parameters are recorded in table-5. The average regression coefficient ($R^2= 0.9919$) near to unity and the adsorption parameter ' α ' are positive suggest that the attractive behavior of the inhibitor on the surface of oil and gas pipeline steel.

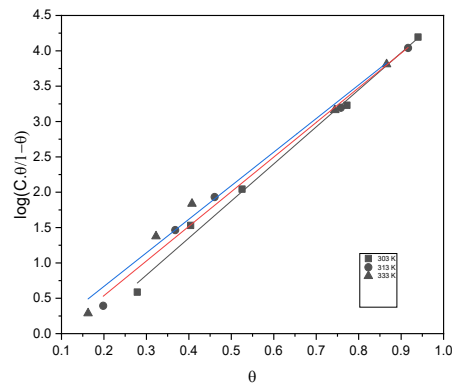


Fig-8. Frumkin isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

3.6.5. Freundlich Isotherm

The Freundlich adsorption isotherm can also be applied using equation (16)

$$\theta = Kc^{1/n} \quad \rightarrow(16)$$

The linear form of Freundlich isotherm equation is as follows

$$\log \theta = \log K + 1/n \log C \quad \rightarrow(17)$$

where k is adsorption capacity (L/mg) and $1/n$ is adsorption intensity and also indicates the relative distribution of the energy and the heterogeneity of the adsorbed sites. This can be plotted as $\log \theta$ vs. $\log C$ and the parameters are shown in table-5. From the slope and intercept, n and K are obtained. The values of K indicate that the inhibitor is strongly adsorbed on the metal surface and ' n ' gives an indication on the favorability of adsorption. It is generally stated that values of ' n ' in the range 2-10 represent good, 1-2 moderate and less than 1 poor adsorption characteristics. Thus the adsorption of MQ inhibitor on oil and gas pipeline steel is good by physical process, since its " n " value in the range 2.7315 to 3.7624.

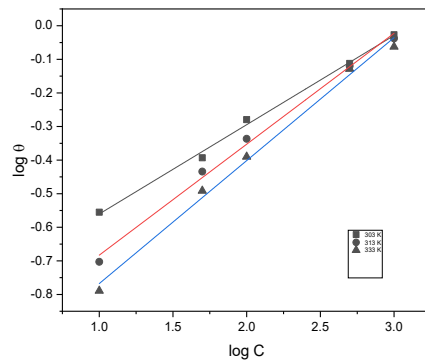


Fig -9. Freundlich isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

3.6.6. El –Awady Isotherm

The El-Awady adsorption isotherm is given by $\log(\theta/1-\theta) = \log K + y \log C$ ----- $\rightarrow (18)$

Where C is the concentration of inhibitor in the bulk solution, ‘θ’ is the degree of surface coverage, K is an El-Awady isotherm constant, equilibrium constant of an adsorption process $K_{ads} = K^{1/y}$ and y represents the tendency of adsorbate occupying a given active site. Value of 1/y less than unity implies the formation of multilayer on the metal surface, while the value of 1/y greater than unity reveals that a given inhibitor occupy more than one active site Curve fitting of the data to the thermodynamic/kinetic model [El-Awady] is shown in fig - 10. . The calculated k_{ads} and 1/y from the El-Awady et al isotherm model is listed in Table-5.

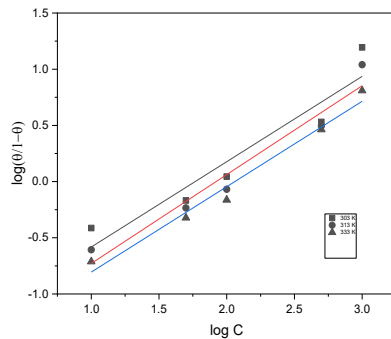


Fig-10. El-Awady isotherm for adsorption of ethanol extract of MQ on the surface of oil and gas pipeline steel

Table – 5: Derived adsorption parameters of MQ on oil and gas pipeline steel

Adsorption Isotherm	Temperature in K	R ²	K	ΔG _{ads} kJ/mol	Variables
Langmuir	303	0.9996	6.7003	-9.6384	-
	313	0.9989	10.3110	-10.4880	
	333	0.9980	13.6050	-11.4691	
Temkin	303	0.9674	0.4751	-14.6490	a 3.4621
	313	0.9765	0.2588	-14.1268	3.1801
	333	0.9714	0.1976	-14.6552	3.1643
Florry-Huggins	303	0.7982	0.0180	-10.2240	x 1.1897
	313	0.8601	0.0142	-10.5388	1.2363
	333	0.9102	0.0128	-11.2035	1.4462
Frumkin	303	0.9941	0.4754	-11.1665	α 2.6200
	313	0.9941	0.6428	-12.6196	2.4495
	333	0.9875	0.7529	-14.4586	2.3739
Freundlich	303K	0.9966	0.1492	-10.9853	n 3.7624
	313	0.9956	0.0970	-11.0350	3.0274
	333	0.9941	0.0735	-11.5903	2.7315
El-Awady	303	0.9031	0.0455	-10.3837	1/y 1.3167
	313	0.9496	0.0302	-10.6347	1.2644
	333	0.9772	0.0272	-11.2951	1.3154

3.7. Thermodynamic Parameters

The another form of transition state equation which is derived from Arrhenius equation (4) is shown below -19

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \rightarrow (19)$$

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation and ΔH the enthalpy of activation. A plot of log (CR/T) vs. 1/T gives a straight line shown in Fig-11 with a slope (-ΔH/R) and an intercept [log(R/Nh) + (ΔS/R)], from which the values of ΔS and ΔH are calculated and listed in Table-6. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult. The entropy (ΔS) is generally interpreted with disorder which may take place on going from reactants to the activated complex.

Table - 6: Thermodynamic parameters of oil and gas pipeline steel in 1.0N HCl obtained from massloss measurements.

S.No	Concentration of MQ in ppm	ΔH (kJ mol ⁻¹)	ΔS (J k ⁻¹ mol ⁻¹)
1	0	--	--
3	10	17.88	0.0231
4	50	9.74	0.0419
5	100	12.72	0.0301
6	500	4.19	0.0544
7	1000	24.49	-0.0056

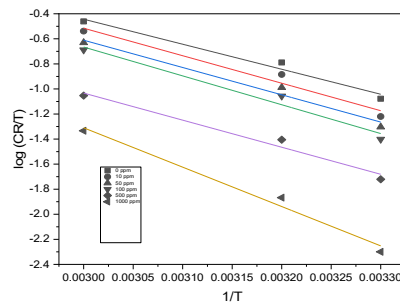


Fig-11. Transition plot of oil and gas pipeline steel in 1.0 N HCl comprising MQ with various temperatures

3.8.ELECTROCHEMICAL MEASUREMENTS

3.8.1. Polarisation Studies

The potentiodynamic polarization curves for oil and gas pipeline steel in 1.0N HCl in the presence and absence of different concentration of MQ extract are shown in Fig-12. The various electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), and Tafel constants (b_a and b_c) are given in Table- 7. It is observed that the presence of MQ extract lowers the corrosion current density (I_{corr}) from 3097 to 281.8 μ A/cm². This significant reduction in corrosion current density clearly indicates that decrease in corrosion rate in the presence of inhibitor. The corrosion potential (E_{corr}) was shifted to nobler direction -494 to -500mV. The percentage of inhibition efficiency increased with increase of inhibitor concentration. This may be attributed to the formation of barrier film due to the adsorption of inhibitor molecules on metal surface involving interactions between π - electrons of inhibitor molecules and vacant d-orbital's of metal ion.

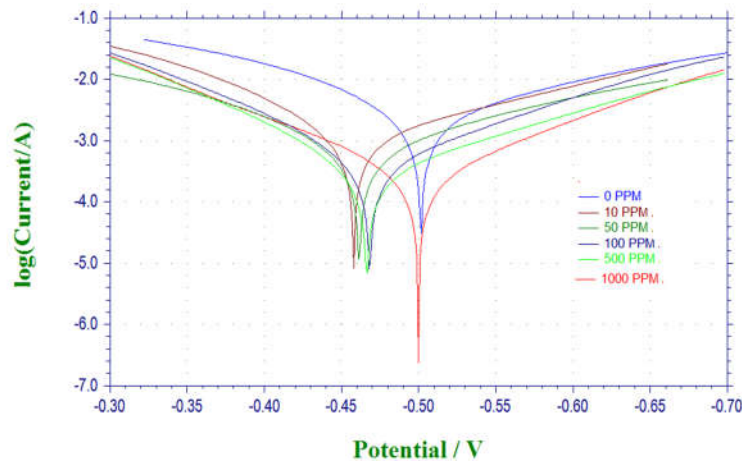


Fig-12. Polarisation curves for oil and gas pipeline steel in 1.0N Hydrochloric acid containing various concentration of MQ inhibitor

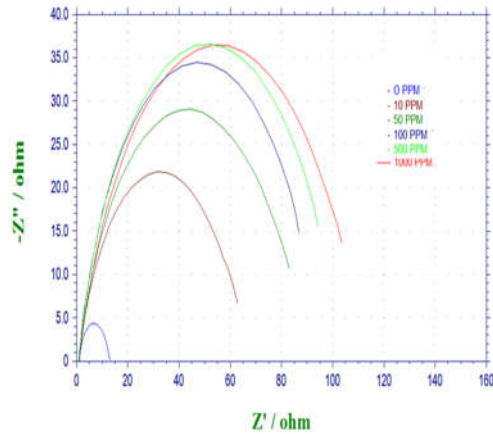
3.8.2. Electrochemical Impedance (EIS) Studies

Fig - (13(a)) shows that the Nyquist plot of oil and gas pipeline steel in 1.0N HCl in the presence and absence of various concentration of MQ inhibitor. The values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were evaluated and their values are given in Table-7. The values of R_{ct} increased from 12.00 to 109.18 Ωcm^2 and C_{dl} decreased with addition of inhibitor concentration. The increase in R_{ct} value is attributed to the formation of stable protective film on the metal-solution interface. The higher values of R_{ct} reflected that the stable passive layer formed at the inhibitor-electrode interface junction and the effective barrier behavior of the inhibitor coating, which may limits diffusion of corrosive species towards the underlying metal substrate.

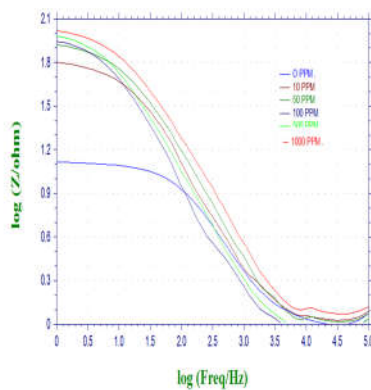
Table- 7 Parameters derived from electrochemical measurements of oil and gas pipeline steel in 1.0N Hydrochloric acid containing various concentration of MQ inhibitor.

Con.of inhibitor in ppm	Polarization measurements					Impedance measurements		
	$-E_{corr}$ mV/decade	b_a (mV/decade)	b_c (mV/decade)	I_{corr} $\mu\text{A cm}^2$	% I.E	R_{ct} (Ωcm^2)	C_{dl} μFcm^2	% I.E
0	494	120.71	143.99	3097	---	12.00	21.46	---
10	459	105.56	161.68	1409	54.50	63.66	80.64	81.15
50	462	125.60	151.40	833.8	73.08	86.46	42.75	86.12
100	469	93.96	114.89	464.2	85.01	90.93	38.62	86.80
500	469	89.02	130.63	333.6	89.23	101.9	31.01	88.13
1000	500	108.39	103.95	281.8	90.90	109.18	26.76	89.01

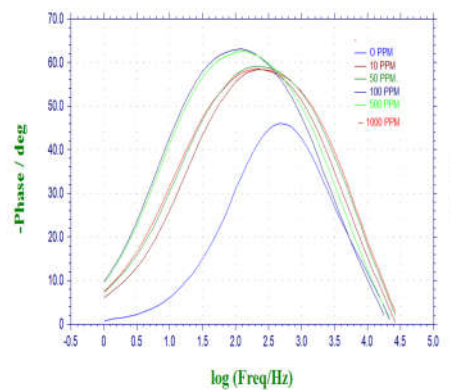
Fig-13 (b) and (c) shows that the Bode impedance and Bode phase angle plot for inhibitor coated and uncoated oil and gas pipeline steel in 1.0N Hydrochloric acid medium at room temperature. It is observed that the impedance of the interface increased with increase of inhibitor concentration and observed maximum phase angle in Fig-13 (c), which may clearly indicates that the prevention of further corrosion process.



(a)



(b)



(c)

Fig-13.(a-c) Electrochemical impedance plots, Nyquist (a), Bode impedance (b), Bode phase angle for oil and gas pipeline steel in 1.0N Hydrochloric acid containing various concentration of MQ inhibitor

4. CONCLUSION

The investigated Marsilea Quadrifolia (MQ) extract on oil and gas pipeline steel has shown excellent inhibition performance in 1.0N Hydrochloric acid environment. The inhibition efficiency increased with the increase of inhibitor concentration and the maximum efficiency 90.44% is achieved. Also, the inhibition efficiency decreased with rise in temperature i.e., from 93.99% at 303K to 86.58 at 333 K. It follows physical adsorption process. Thermodynamic parameter viz., activation energy (E_a) and standard free energy of adsorption (ΔG_{ads}) suggests that physisorption is spontaneous. The MQ inhibitor obeys Langmuir adsorption isotherm. Also, the inhibition efficiency is found to be 89.01% and 90.90% by

impedance and polarization studies. This study also showed that MQ functioned as a mixed-type corrosion inhibitor in the acid environment

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