INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

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*Corresponding author.

Tel: +91 975 043 5441
chemthiru@yahoo.in

Corrosion inhibition behaviour on carbon steel in well-water by Ethanolic extract of *Portulaca quadrifida* (Chicken weed) leaves

P Thirupathi[1]*, B R Venkatraman[1]

1 PG & Research Department of Chemistry, Periyar E.V.R. College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli, 620 023, Tamilnadu, India. Tel.: +91 975 043 5441

Abstract

Objectives: To evaluate the corrosion inhibition of an ethanolic extract of *Portulaca quadrifida* (PQ) leaves on the carbon steel surface in well-water by using a weight-loss study with various immersion periods, temperatures, and pH. The kinetic and thermodynamic parameters are calculated for various temperatures. **Methods:** The protective film has been analyzed by using SEM, EDX and AFM studies. The inhibition action of PQ extract was analyzed by potentiodynamic polarization study, the electrochemical impedance studies are used to the analysis the protective layer formed on the carbon steel surface. **Findings:** The maximum inhibition efficiency is found to be 92% for 500ppm of PQ and 30ppm of Zn^{2+} ions at 303K. The synergistic effect exists between ethanolic extract of *Portulaca quadrifida* leaves and Zn^{2+} ions by synergistic parameters. The ethanolic extract of PQ leaves acts as a mixed-type inhibitor. The activation energy (E_a) values indicate that the adsorption of PQ leaves extract on the carbon steel surface. The enthalpy of adsorption (ΔH) values suggests that the reaction is endothermic. The free energy of adsorption (ΔG_{ads}) values is negative and less than the $-20 KJmol^{-1}$. The negative values of ΔS_{ads} are confirmed to form an ordered stable layer of the inhibitor molecule on the carbon steel surface as well as a stable equilibrium between the adsorption and desorption processes. The adsorption isotherm is best fitted with the Langmuir model. **Novelty:** The ΔG_{ads} values indicate that the adsorption of inhibitor on the carbon steel surface belongs to the physisorption as well as the adsorption layer has an electrostatic character. The adsorption process of the inhibitor is spontaneous. The thermodynamic parameters give a strong interaction between the inhibitor molecules and carbon steel surface. Four adsorption isotherms including Langmuir, El-Awady, Flory-Huggins, and Temkin models, investigate the mode of inhibition of PQ leaves extract.

Keywords: Carbon steel corrosion; weightloss study; electrochemical studies; Ftest; synergistic effect; SEM; EDX; AFM; adsorption isotherms

1 Introduction

Corrosion is a natural process in which an unstable metal is transformed into a chemically stable form, such as oxide and hydroxide forms by the mineral chemically or the electrochemical with the surrounding environment[1]. Corrosion is an undesirable phenomenon as it destroys the beneficial properties of the mineral[2]. Because of corrosion many useful properties of metal like malleability, ductility, and electrical conductivity is lost. Synthetic organic compounds are widely used as corrosion inhibitors for the prevention of corrosion of the many metals and alloys in various aggressive environments. Due to their hazardous nature, researchers focus their attention on developing cheap, non-toxic, biodegradable, and environment-friendly natural products of plant origin as corrosion inhibitors[3–12]. The inhibition proficiency of synthesized or natural organic compounds principally depends on the structure and trait of the adsorbed layer on the low-carbon steel[13–24]. Availableness of the unshared or π-electrons in inhibitor structure encourages the exchange from the inhibitor to the low-carbon steel due to the vacant d-orbital for the transition elements and therefore the formation of the coordination bond. Coordination bonds, including the exchange of electrons between inhibitor-molecules and therefore the surface of the metal, might occur. Traditional corrosion inhibitors contain chemical compounds that can have toxicological effects and pose harmful impacts on the receiving environment, especially surface waters[25]. Therefore, eco-friendly corrosion inhibitors also known popularly as green alternatives to replace toxic and hazardous chemicals are studied extensively in recent years[26–28]. Among all the green alternatives, the utilization of corrosion inhibitors obtained from plant extracts has continued to draw in interest thanks to their low human and environmental toxicity. Compared to synthetic inhibitors, plant extract-based corrosion inhibitors also cost less, and may easily be mass-produced if necessary[29]. The plant extract-based additives are used for rust mitigation in armors even during the medieval period[30,31].

2 Experimental methods

2.1 Composition and preparation of specimen

The percentages of composition for carbon steel specimen are P 0.06%, Mn 0.4%, S 0.0267%, C 0.1% and Iron 99.287%. The carbon steel sheet is cut into 1.5cm x 3.5cm x 0.2cm for weightless measurement. The carbon steel was polished using Allen paper 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0. The impurities using double distilled water and acetone, dried and kept in a desiccator then weighing accurately by a digital balance [Shimadzu Ay 62]

2.2 Preparation of the *Portulaca quadrifida* Extract

By refluxing 10g of dried *Portulaca quadrifida* tends to leave in presence of 200ml of ethanol for 3h, the plant extract is prepared and then filtered off using whatmann filter paper. By using distilled water, these crude extracts were dried and then a dense solid mass was obtained. 1g of Pisonia alba crushed up leaves has been decided to make with a 100ml Standard Measuring Flask with double distilled water up to the mark. Various amounts of leaves extracts are decided to make from this solution. The major active compound obtained from an ethanolic extract of PQ leaves is shown in Figure 1.

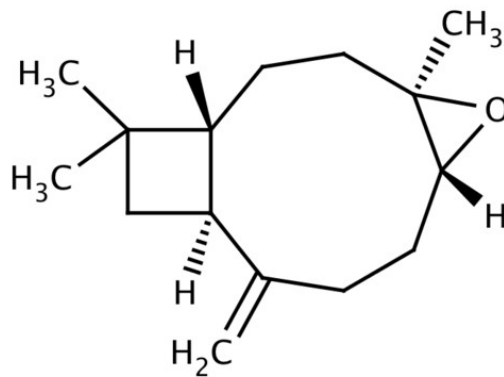**Beta Caryophyllene Oxide**

Fig 1. Major active component observed in ethanolic extract of *Portulaca quadrifida* leaves

2.3 Weight loss study

The carbon steel specimens are immersed in well water with and without various inhibitor concentrations. After the immersion the carbon steel is removed from various test solution, thoroughly washed with double distilled water, dried well and weighted accurately again. From the average weight-loss, the inhibition efficiency[32] and corrosion rate[33–35] are calculated using the following equations.

$$IE\% = \frac{W_{BLANK} - W_{INHIBITOR}}{W_{BLANK}} \times 100$$

$$Corrosion\,Rate(mmpy) = \frac{87.6 \times Weight\,loss\,(mg)}{D \times A \times T}$$

2.4 Electrochemical studies

Polarization and electrochemical impedance studies are carried out using CHI electrochemical impedance analyzer (model 760D) a universal programmer in a conventional three-electrode glass cell. The working electrode is a rectangular specimen of carbon steel with one face of the electrode (km^2 area) exposed and the rest shielded with red lacquer, a rectangular platinum foil act as a counter electrode and a saturated calomel electrode (SCE) is used to the reference electrode. From the polarization curves, corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes values are calculated. A time interval of 10 to 15 minutes is given for the system to attain a steady-state open-circuit potential. From the AC-impedance study, the double layer capacitance and charge transfer resistance values are calculated using An AC frequency range from 0.1 Hz to 100 kHz.

The inhibition efficiency is calculated using the following equations[36]

From polarization study,

$$IE\% = \frac{I_{corrosion(blank)} - I_{corrosion(inhibitor)}}{I_{corrosion(blank)}} \times 100$$

From AC impedance study,

$$IE\% = \frac{R_{ct(inhibitor)} - R_{ct(blank)}}{R_{ct(inhibitor)}} \times 100$$

2.5 SEM analysis

The surface morphology analysis for the polished, corroded area and protective layer on carbon steel surface was examined by JEOLMODEL 6390 SEM.

2.6 Synergistic effect

The carbon steel immersed in well water contains various concentration of PQ with Zn^{2+} ions. The synergism parameters are used to determine the synergistic effect existing between plant extract and Zn^{2+} ions

The synergism parameters are calculated using the following formula[37]

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$$

Where, q_1 and q_2 are surface coverage, q'_{1+2} is cumulative surface coverage

2.7 F-study

F-analysis is used to determine the inhibitor system statistically significant or not through synergistic effect between plant extract and Zn^{2+} ions

2.8 AFM Technique

Atomic force microscope study was utilized to surface morphology on the carbon steel in well water contains various concentration of PQ with Zn^{2+} ions using the Veeco dinnova model with a scan rate of 0.6 Hz/ second
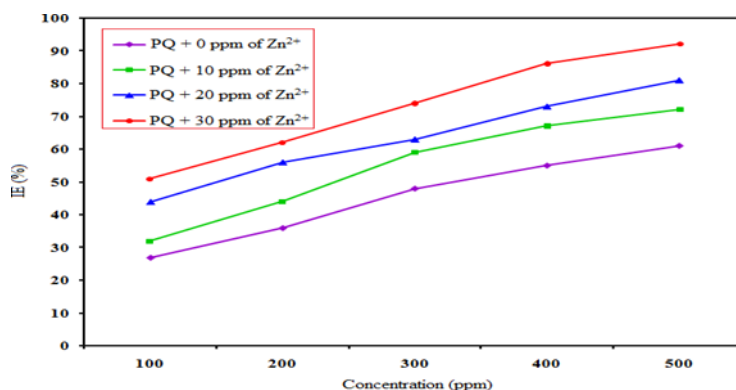
3 Result and Discussions

3.1 Weight-loss Measurement

The corrosion inhibition effects of an ethanolic extract of *Portulaca quadrifida* over carbon steel immersed in well water contain Zn^{2+} ions are studied. The weight-loss study was utilized to calculate the inhibition efficiency and corrosion rate for carbon steel immersed in well water containing various concentrations of PQ Zn^{2+} system for one day immersion period. The results are given in Table 1. The various concentrations of PQ with and without Zn^{2+} ions are plotted in Figure 2 .

Table 1. Determination of IE and CR of PQ- Zn^{2+} system (Period of immersion:1 day)

| PQ (ppm) | I.E % | | | | CR (mmpy) | | | |
| | Zn^{2+} (ppm) | | | | Zn^{2+} (ppm) | | | |
	0	10	20	30	0	10	20	30
0	-	13	26	31	0.1809	0.1574	0.1339	0.1249
100	27	32	44	51	0.1320	0.1230	0.1013	0.0886
200	36	44	56	62	0.1158	0.1013	0.0796	0.0687
300	48	59	63	74	0.0941	0.0742	0.6693	0.0470
400	55	67	73	86	0.0814	0.0597	0.0488	0.0253
500	61	72	81	92	0.0706	0.0507	0.0344	0.0145

The inhibition efficiency increased from 27% to 61% for various concentration of PQ in absence of Zn^{2+} ions. The combination of various concentration of PQ and 10ppm Zn^{2+} gives the inhibition efficiency from 13% to 72% and also corrosion rate from 0.1574 to 0.0507. The concentration of PQ and 20ppm of Zn^{2+} system gives the inhibition efficiency from 26% to 81% as well as corrosion rate 0.1339 to 0.0344. The formulation of various concentration of 500ppm PQ and 30ppm of Zn^{2+} system gives the optimum inhibition efficiency from 31% to 92% and also corrosion rate decreased from 0.1249 to 0.0145. Therefore, it is evident that the inhibition efficiency increases with its concentration, which is due to the adsorption of the metallic complex on the carbon steel surface[38]. The fact that the metal surface area covered by the inhibitor surface coverage increases with its concentration supports the idea that the decrease in corrosion rate is due to the inhibitor adsorption on the carbon steel surface to form a protective corrosion product layer due to the existence of hetero cyclic compound is shown in Figure 1[39]. The mixture of inhibitors (PQ-Zn^{2+}) has better IE than individual inhibitors[40–42].

Fig 2. Influence of Immersion Period on the IE and CR for PQ- Zn^{2+} System

The above graph indicated that the IE% increases, when the concentration of PQ and Zn^{2+} ions are increased from 100ppm to 500ppm (PQ) and (0ppm to 300ppm)

3.2 Thermodynamic parameters

The free energy of adsorption (ΔG_{ads}), the heat of adsorption (q_{ads}), and entropy of adsorption (ΔS_{ads}) values give the nature of adsorption on the metal surface. These values are shown in Table 2. The ΔG_{ads}, q_{ads} and ΔS_{ads} values are negative in sign. These negative values indicate that the adsorption of inhibitor systems has a spontaneous process with a high stability of the adsorbed film on the carbon steel surface due to physisorption [43,44]. These negative ΔG_{ads} values are less than -20kJmol^{-1}, therefore, the nature of adsorption for PQ leaves is physisorption at all various temperatures. The negative values of ΔS_{ads} indicate that the adsorbed molecules (corrosion products) on the corrosion steel surface are ordered than in the solution (corrosion reactants) [1]. The thermodynamic corrosion parameters are calculated using following equations.

The free energy of adsorption was calculated using the following equation [45].

$$\triangle G_{ads} = 2.303RT log(55.5K_{ads})$$

Where, 55.5 is the molar concentration of water in solution and

$$K_{ads} = \frac{\theta}{C(1-\theta)}$$

The heat of adsorption was calculated using the equation [33]

$$q_{ads} = 2.303R \left[\left(\frac{\theta_{T2}}{1-\theta_{T2}} \right) - log \left(\frac{\theta_{T1}}{1-\theta_{T1}} \right) \left(\frac{T_1 T_2}{T_2 - T_1} \right) \right]$$

θ_{T1} is the surface coverage at lower temperature (T_1), θ_{T2} is the surface coverage at higher temperature (T_2)

The entropy of adsorption (ΔS_{ads}) was calculated using the below relationship [1]

$$\triangle S_{ads} = \frac{q_{ads} - \triangle G_{ads}}{T}$$

Table 2. Effect of thermodynamic parameters on the adsorption process

Inhibitor system	Temperatures (K)	ΔG_{ads} (KJ/mol)	q_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol)	K_{ads}
PQ	303	-18.0	-32.5	-0.167	23.0
	313	-17.4	-26.5	-0.141	14.7
	323	-16.7	-38.7	-0.172	9.1
	333	-16.1	-32.7	-0.147	6.0

3.3 Kinetic parameters

The E_a value is found to be 17.14KJ/mol for the blank system. This value was increased by the presence of the inhibitor. Ea for PQ leaves extract is 101.0KJ/mol at 500 ppm systems. E_a values greater than 80KJ/mol are consistent with chemisorption, while Ea values lower than 80KJ/mol followed physisorption [32]. Therefore, Ea values indicate that the chemisorption on the carbon steel surface. The ΔH value was increased from 14.6KJ/mol to 98.5 KJ/mol for combined inhibitor (blank to 500ppm) systems, The high positive ΔH values of PQ leaves indicate that the reactions are endothermic [46] for corrosion processes of carbon steel in well-water. The results are given in Table 3. The Kinetic parameters are calculated using following equations.

The activation energy (E_a) values are calculated using the following Arrhenius equation [32]

$$E_a = 2.303R log \left(\frac{C_{RT1}}{C_{RT2}} \right) \left[\frac{T_1 T_2}{T_2 - T_1} \right]$$

C_{RT1} is the corrosion rate of the lower temperature (T_1), C_{RT2} is the Corrosion rate at the higher temperature (T_2), and R is gas constant (8.314 J/mol)

The enthalpy change (ΔH) values are calculated using following equation [46]

$$\triangle H = E_a - RT$$

Table 3. Effect of kinetic parameters on the corrosion process

Concentration of combined inhibitor	Ea KJ/mol	ΔH KJ/mol
Blank	17.1	14.6
100	54.2	51.7
200	57.8	55.2
300	59.7	57.1
400	72.2	69.6
500	101.0	98.5

3.4 Effect of pH on PQ- Zn2+System:

The effect of pH changes on PQ Zn^{2+} system in well water containing 500ppm of PQ and 30 ppm of Zn^{2+}. The inhibition efficiency and corrosion rate are calculated using weight loss measurement. The results are given in Table 4.

Table 4. Influence of pH on IE and CR for PQ-Zn^{2+} inhibitor system (Period of Immersion: one day)

System	pH		
	3	8	12
Well-water CR (mmpy)	0.2067	0.1809	0.1912
PQ-Zn2+ system (500:30 ppm) CR (mmpy)	0.0537	0.0145	0.0229
IE (%)	74	92	88

The maximum inhibition efficiency of 92% was obtained at pH of 8 for PQ-Zn^{2+} system. The inhibition efficiency was decreased from 92% to 74% when the pH is reduced from pH 8 to 3 by the addition of dilute HCl. The addition of NaOH to PQ-Zn^{2+} system (pH =8), the pH is decreased from 92% to 88% as well as corrosion rate is increased[47,48].

3.5 Effect of Immersion Period on PQ- Zn2+System

The effect of immersion period from 1to 7days on the corrosion inhibitor inhibition behaviour carbon steel in well-water contains a various concentration of PQ with Zn^{2+} ions, the inhibition efficiency and corrosion rate was calculated using weight study. The results are given in Table 5. The inhibition efficiency behaviour and immersion period are plotted in Figure 3.

Table 5. Effect of Immersion Period on PQ- Zn^{2+} System

Immersion Period (days)	Corrosion Rate		IE%
	Well-water (mmpy)	PQ- Zn2+ (500:30ppm)(mmpy)	
1	0.1809	0.0145	92
3	0.2013	0.0241	88
5	0.2124	0.0404	81
7	0.2158	0.0647	70

From the above result, the inhibition efficiency was decreased from 92% to 70% as well as corrosion rate increased from 0.1809 to 0.2158 in well-water and absence of PQ-Zn^{2+} system, from 0.0145 to 0.0647 in presences of PQ-Zn^{2+} system. Therefore, the effect of immersion period on an ethanolic extract of plant leaves confirmed that the protective layer formed on the metal surface deteriorates and dissolves in the solution by the corrosion environment and enhances the corrosion process[49,50].
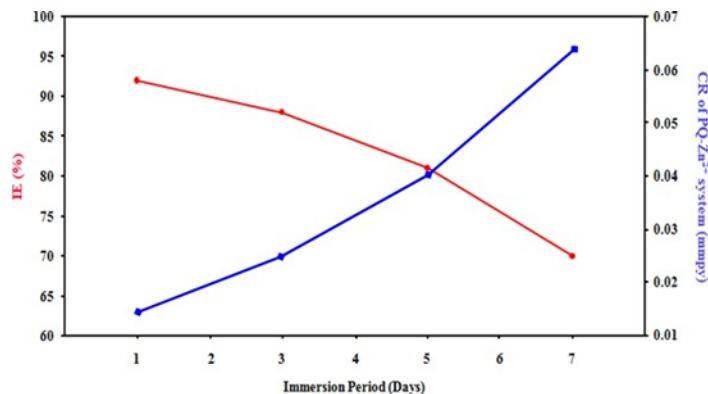
Fig 3. Influence of Immersion Period on the IE and CR for PQ- Zn^{2+} System

3.6 Synergism Parameter

The synergistic effect exists between the various concentration of PQ and 30ppm of Zn^{2+} ions. SI values approaches 1 when no interaction between the inhibitors. SI < 1, synergistic effect exists between the two inhibitors[51–53]. Therefore, the synergistic inhibition effect was the improved performance of a mixture of inhibitors compared with the individual inhibitors[37]. The results are given in Table 6.

Table 6. Synergism Parameters for PQ-Zn^{2+} System

PQ (ppm)	Zn^{2+} (30 ppm)	q_1	q_2	q'_{1+2}	S_I	IE %
100	30	0.27	0.31	0.51	1.0280	51
200	30	0.36	0.31	0.62	1.1621	62
300	30	0.48	0.31	0.74	1.3800	74
400	30	0.55	0.31	0.86	2.2179	86
500	30	0.61	0.31	0.92	3.3638	92

3.7 F-Study

F-Study was used to identification of the synergistic effect existing between the various concentration of PQ and Zn^{2+} has statistically significant or not[54–56]. The results are given in Table 7.

Table 7. F-value distributedbetween the IE of PQ- Zn^{2+} System

Zn^{2+} (ppm)	Level of Significance of F	source of variance	sum of square	degree of freedom	mean square	F-values
10	P> 0.05	Between	220.9	1	220.9	0.95
		Within	1868	8	233.5	
20	P> 0.05	Between	810	1	810	4.04
		Within	1602.4	8	200.3	
30	P> 0.05	Between	1904.4	1	1904.4	8.11
		Within	1878.2	8	234.8	

To examine where the effect of Zn^{2+} on the inhibition efficiencies of PQ is statistically significant F-study was carried out. The obtained F-value 0.95, 4.04 for 10ppm 20ppm of Zn^{2+} is not statistically significant. Hence it is less than the critical F-value 5.32 for 1.8 degree of freedom at 0.05level of significance, therefore it is concluded that the effect of 10ppm, 20 ppm of Zn^{2+} on the inhibition efficiencies of different concentration of PQ is not statistically significant[57]. The obtained F-value 8.11 for 30ppm of Zn^{2+} has statistically significant. Since, it is greater than the critical F-value 5.32 for 1.8 degree of freedom at 0.05level of significance. Therefore, it is concluded that the effect of 30ppm of Zn^{2+} on the inhibition efficiencies of different concentrations of PQ is statistically significant[57].

3.8 Analysis for Polarization Curves

Polarization curves was used to calculate the corrosion parameters such as corrosion potential (E_{corr}), Tafel slopes, (b_a, b_c) linear polarization resistance and corrosion current Icorr values. The results are given in Table 8. When carbon steel is immersed in well-water, the corrosion potential is -580mV vs SCE, the corrosion current is 5.5431μA/cm^2. When carbon steel is immersed in well-water containing 500ppm of PQ and 30ppm of Zn^{2+}, the corrosion potential is shifted from -580 to -603mV vs SCE. There is not much change in the corrosion potential value, it is concluded that the inhibitor system act as a mixed type of inhibitor, if the displacement in E_{corr} value is > 85mV, the inhibitor can be seen as a cathodic or anodic type inhibitor; if the displacement of E_{corr} value is < 85mV, the inhibitor can be seen as mixed type. In the present study the maximum displacement in E_{corr} was much lower than 85mV suggesting that PQ leaves extract is a mixed type with predominance of cathodic inhibition[58]. It is confirmed that the cathodic reaction is controlled predominantly as well as the corrosion current decreases from 5.5431μA/cm^2 to 1.0250μA/cm^2 and linear polarization value increase from 963 to 3130Ω cm2. It is indicating the formation of safe layer on the metal surface[59]. The polarization curves of carbon steel immersed in well water with and without inhibitors are given in Figure 4. The anodic slope value was increased from 116.23mV/dec to 201.90mV/dec and the cathodic slope value is increases from 110.88mV/dec to 198.52mV/dec. Hence, anodic slope is greater than cathodic slope. Therefore, it is indicated that the inhibitor system behaves as a mixed type inhibitor[60] but the anodic reaction is more controlled on the anodic side polarization than on the cathodic side polarization[61].

Table 8. PolarizationParameters for PQ- Zn^{2+} System

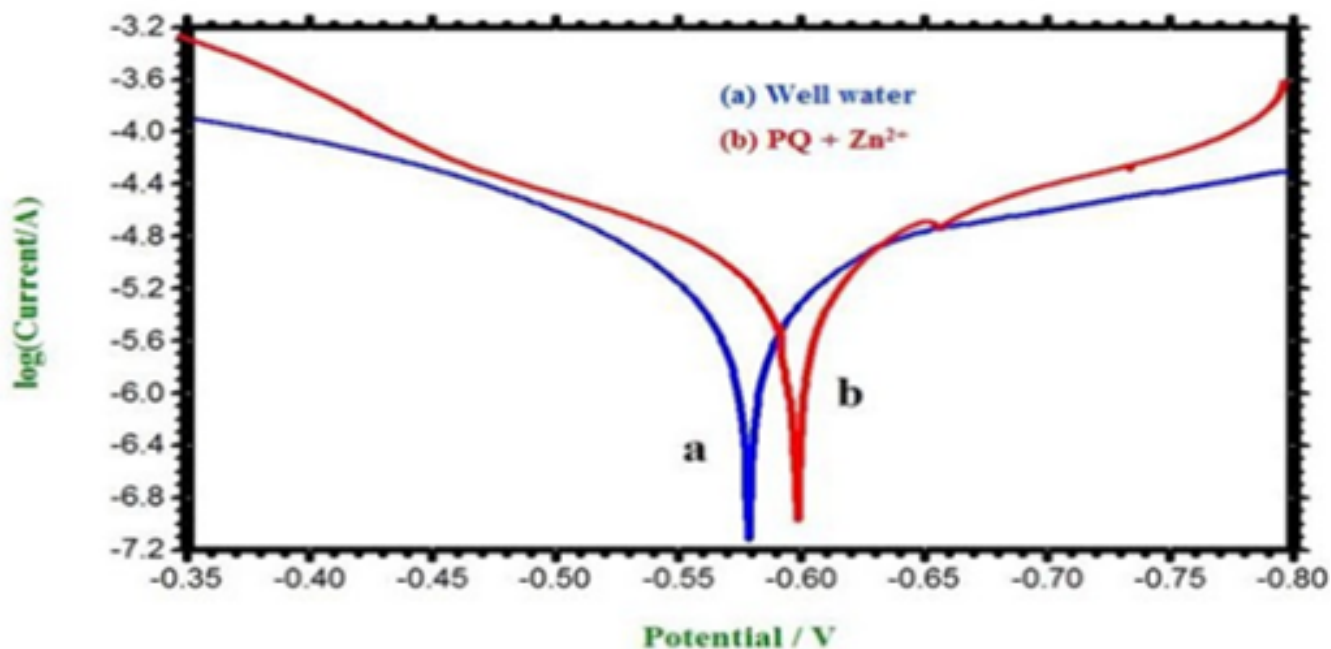| System	E_{corr} (mV)vs SCE	b_a [mV/dec]	b_c (mV/dec)	LPR (Ω cm2)	I_{corr} μA/cm^2
Blank (well-water)	-580	116.23	110.88	963	5.5431
PQ- Zn^{2+} (500:30 ppm)	-603	201.90	198.52	3130	1.0250

Fig 4. Tafel Curves for PQ-Zn$_{2+}$ System onto carbon steel in well-water
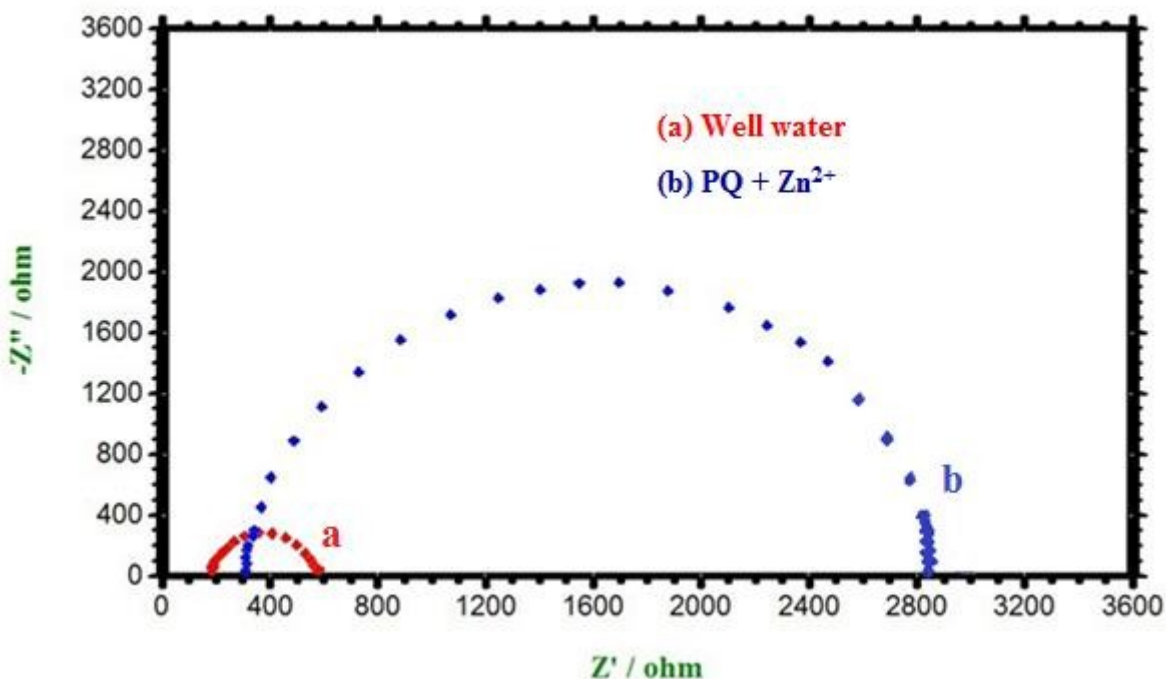
3.9 AC Impedance Spectra

AC impedance spectra are used to accurately confirm the formation of the layer on carbon steel immersed in well-water containing 500ppm of PQ and 30 ppm of Zn^{2+} as well as the calculated charge transfer resistance(R_{ct}) and the double layer capacitance C_{dl}. The results are given in Table 9

Table 9. AC ImpedanceParameters of well-water and PQ-Zn$_{2+}$ System

System	R_{ct} (Ω cm$_2$)	C_{dl} (μF/cm^2)
Blank(well-water)	391	1.3137
PQ-Zn$_{2+}$ (500:30 ppm)	2530	0.0320

The R_{ct} value is 391Ω cm$_2$ and C_{dl} value is 1.3137μF/cm^2, when carbon steel was immersed in well water without inhibitor concentration. When 500ppm of PQ and 30ppm of Zn^{2+} is added to the above system, the R_{ct} value has increased from 391 to 2530Ω cm$_2$ and the C_{dl} value is reduced from 1.3137μF/cm^2 to 0.0320μF/cm^2 this inhibitor system has better inhibition performance on the carbon steel in well water[62]. From the R_{ct} and C_{dl} values, this result indicates that the formation of a protective layer on the metal surface[63]. The AC impedance spectra of the carbon steel immersed in well-water containing 500ppm of PQ and 30ppm of Zn^{2+} are shown in Figure 5.

Fig 5. AC Impedance Spectrafor well-water (a) and PQ-Zn^{2+} System (b)

3.10 Scanning Electron Microscopy technique

Scanning electron microscope was used to understand the nature of the safe layer forming in carbon steel surface in the absence and presence of inhibitors and the extent of corrosion over carbon steel. The SEM images for different Magnification of carbon steel immersed in well water for one day with and without plant leaves extract are given in Figure 6 (a, b, c). From image 6(a), it is indicating the smooth surface of the carbon steel and also the absence of any corrosion products onto the carbon steel surface. From image 6(b), this image indicates the roughness and the highly corroded area forming on carbon steel surface, when carbon steel immersed in well water. From image 6(c), this image shows the reduced corroded area on the carbon steel surface due to the formation of an insoluble complex on carbon steel surface when carbon steel immersed in well-water containing 500ppm of PQ and 30 ppm of Zn^{2+}. The damage of the steel surface has diminished in the presence of the inhibitor and rough, corroded steel surface displaces to much smooth[64]. This is due to the covering of metal surface with a protective layer[35]. The scanning electron microscope images for metal surface are investigated[51,65–68].
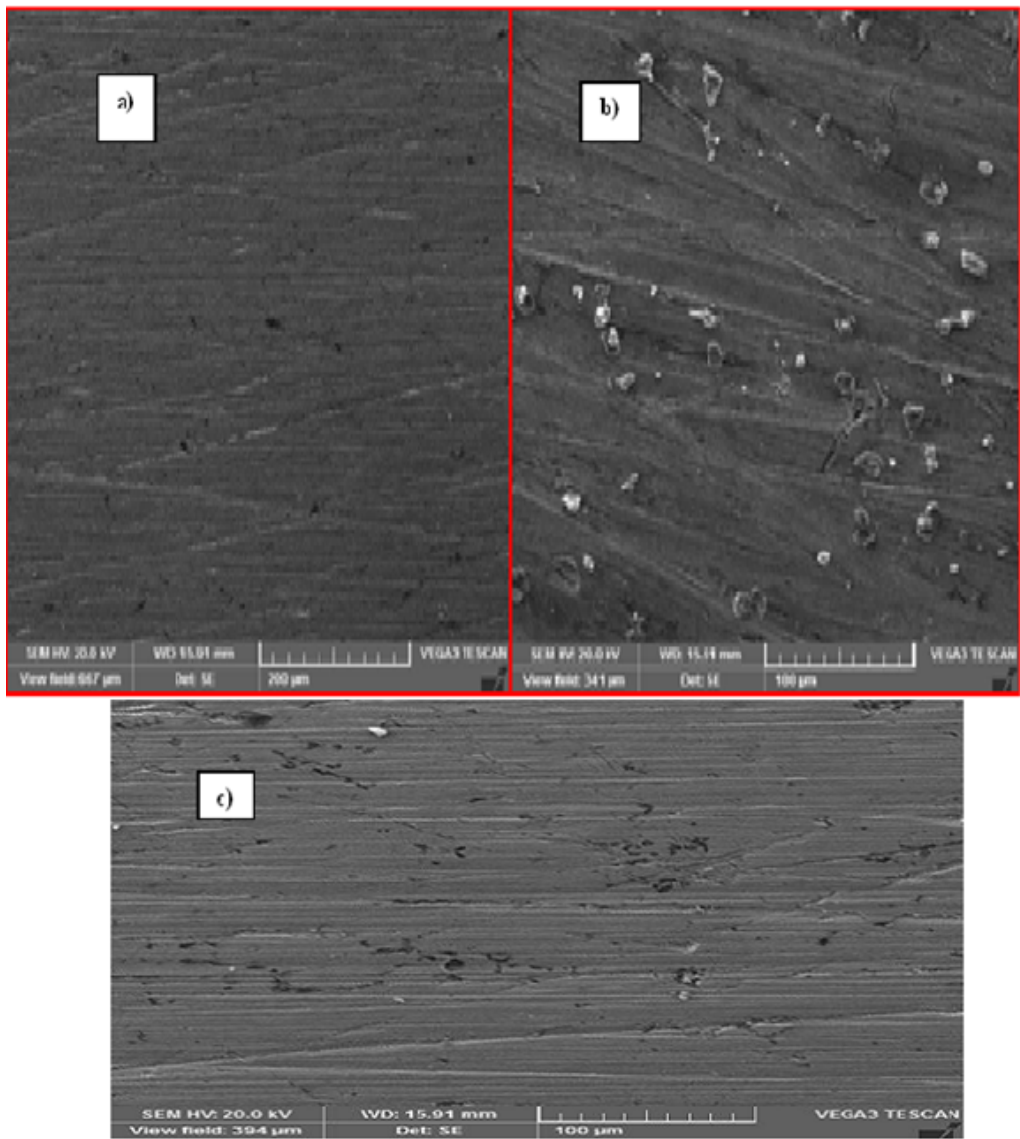
Fig 6. SEM images for Polished-Carbon steel (a), Blank (b), PQ-Za^{2+} system (c)

3.11 Energy Dispersive X-Ray Study

EDAX spectra are used to determine the composition of elements present on the metal surface[68]. The EDAX spectra result indicates that N, O, and C atoms of PQ extract and Zn^{2+} has coordinated with Fe^{2+} resulting in the formation of Fe^{2+}-PQ complex on the anodic side of the metal surface as well as Zn(OH)$_2$ is forming on the cathodic side of the metal surface.
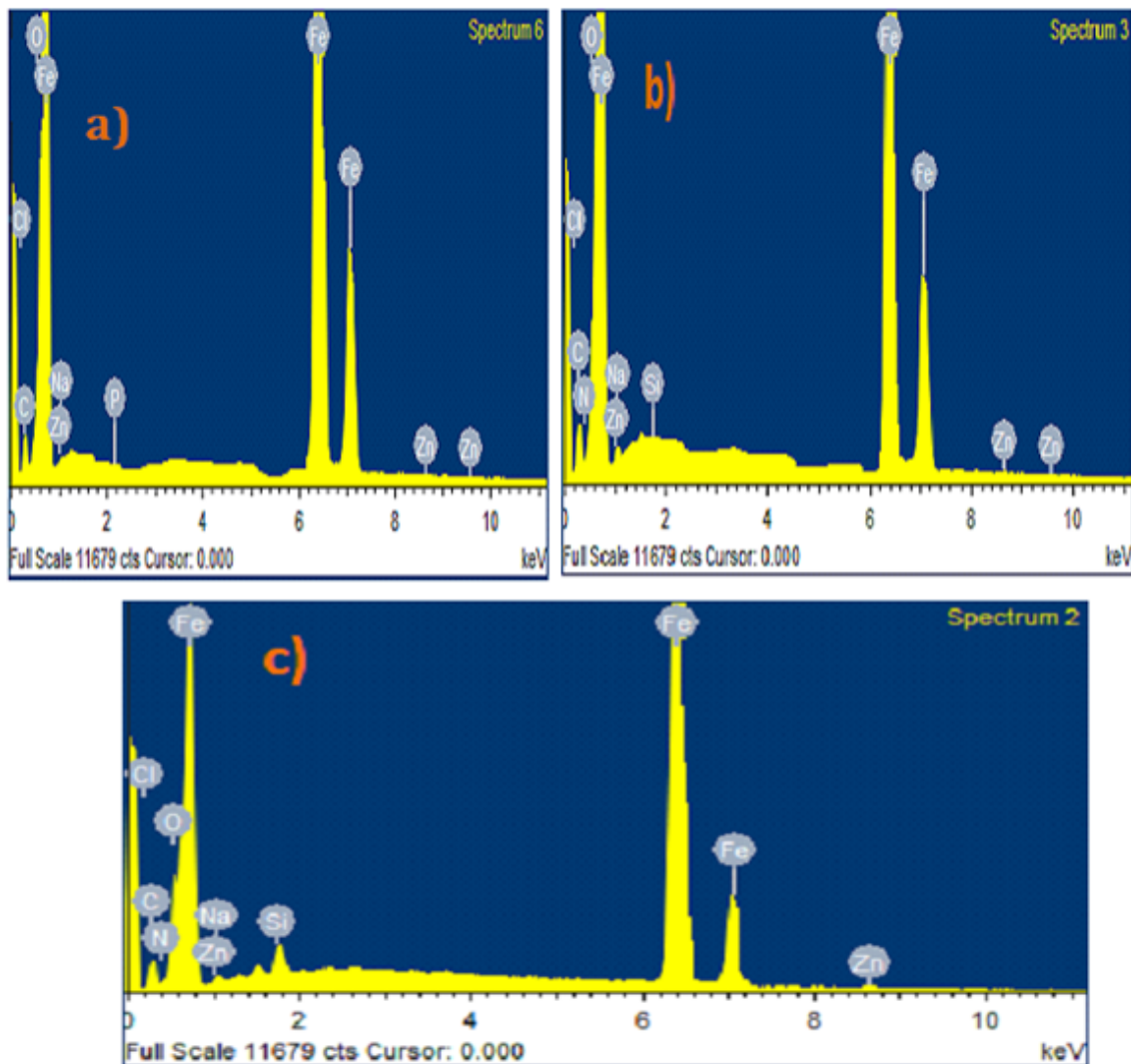
Fig 7. EDX Spectra of Polished carbon steel (a), Blank (b), PQ-Zn^{2+} system (c)

The EDAX spectrum of polished carbon steel is given in Figure 7 (a). This spectrum containing mainly Fe C and O signal. The EDAX spectrum of carbon steel immersed in well-water is shown in Figure 7(b) this spectrum shows the characteristic peaks of elements constituting the carbon steel specimen such as Fe, C, O and Cl etc,. The EDAX spectrum of carbon immersed in well-water Containing 500ppm of PQ and 30ppm of Zn^{2+} is given in Figure 7(c). This spectrum indicating the additional elements present on the carbon steel surface N, O, C, and Zn etc.,
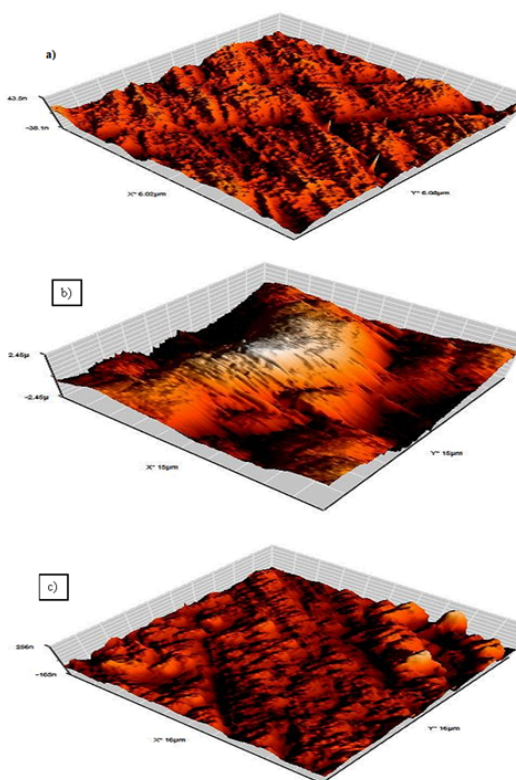
3.12 Atomic Force Microscopy techniques

An Atomic force microscope was used to calculate the Root-mean Square Roughness (R_{rms}), Average Roughness (R_a) and Maximum Peak-to-valley (P-V) height values, when carbon steel immersed in inhibited and uninhibited system. The results are given in Table 10. AFM is a useful technique to examine the surface morphology at nano-micro-scale to analysis the effect of the inhibitor on the generation and the progress of the corrosion at the metal/solution interface[68–70].

The value of Root mean square roughness, Average Roughness and Maximum Peak-to-valley (P-V) height for polished carbon steel are 5.66nm, 6.25nm, and 24.14nm respectively. These values are indicating a more homogeneous surface. The

Table 10. AFM parameters in absence and presence of PQ-Zn^{2+} system

sample	polished carbon steel	well-water (blank)	PQ-Zn$_{2+}$ (500:30ppm) system
Average Roughness (R$_a$) (nm)	5.66	1317.08	12.74
Root mean square roughness (R$_{rms}$) (nm)	6.25	1476.12	17.89
Maximum Peak-to-valley (P-V) height (nm)	24.14	3791.00	102.31

Root mean square roughness, Average Roughness and Maximum Peak-to-valley (P-V) height values for carbon steel immersed in well-water are 13.17nm, 1476.12nm, and 3791.00nm. these values suggest that the producing greater surface roughness compared with polished carbon steel surface, due to rate of corrosion is increases on carbon steel surface in well-water when carbon steel is immersed in well-water containing 500ppm of PQ and 30ppm of Zn^{2+}, the Average Roughness value is reduced to 12.74nm from 1317.08nm, Root mean square roughness (R$_{rms}$) value was decreased to17.89nm from 1476.12nm as well as Maximum Peak-to-valley (P-V) height value reduced to 102.31nm from 3791.00nm, these parameters values are confirmed that the smoother surface appears over carbon steel specimen, due to the produces safe layer (nano-layer)[45] of Fe^{2+}-PQ extract complex and Zn(OH)$_2$ on the carbon steel surface.

Fig 8. AFM 3D images for Polished carbon steel (a), Blank (b), and PQ-Zn^{2+} system (c)

From the above images, Figure 8 (a) for polished carbon steel surface is uncorroded carbon steel surface due to small roughness was obtained on polished carbon steel surface by atmospheric corrosion. Figure 8(b) for carbon steel is immersed in well-water. This image displays highly corroded on the metal surface with maximum roughness area. Figure 8(c) for carbon steel is immersed in well-water containing 500ppm of PQ extract and 30ppm of Zn^{2+}. This AFM image appears smooth on the carbon steel surface due to formation of a protective film on the metal surface[64,71,72]. From the extract, this leads to the reduction of the corrosion of the carbon steel[1].

3.13 Adsorption Isotherms Behaviour

Adsorption isotherm models are used to investigate the possible adsorption mode of an ethanolic extract of PQ leaves by testing the experimental data obtained with four adsorption isotherm models[73]. The relationship between the surface coverage and the inhibitor concentration forms a basis to the study of the mechanism of adsorption isotherm[74]. All these isotherms are represented as follows[75]

$$f(\theta, x)exp(-2a\theta) = KC$$

Where, f(θ, x) is the configurational factor, θ is the surface coverage, C is the concentration of the inhibitor, X is the molecular interaction parameter, and K is the equilibrium constant for the adsorption process.

The Langmuir adsorption isotherm is expressed as follows[35,76].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

EI-Awady adsorption isotherm is represented by using the following equation[77]

$$log\left(\frac{\theta}{1-\theta}\right) = logK + ylogc$$

Where, K_{ads} is equilibrium constant of the adsorption process. It is related to k by

$$K_{ads} = K^{1/y}$$

Flory-Huggins adsorption isotherm is represented by[78]

$$log\left(\frac{\theta}{C}\right) = logK + xlog(1-\theta)$$

Where,

X is the size parameter,

Temkin adsorption isotherm is expressed by following equation[46]

$$\theta = \frac{-2.303logK_{ads}}{2a} - \frac{2.303logC}{2a}$$

Where, a is the lateral interaction parameter. This isotherm graph is drawn by taking θ in the y axis and log c in the x axis.

The data of regression co-efficient (R^2) were 0.997, 0.928, 0.992, and 0.989 for Langmuir, El-Awady, Flory-Huggins, and Temkin models. From the regression co-efficient (R^2) values, the R^2 values of four adsorption isotherm models were almost equal to unity[46]. However, the R^2 value of Langmuir isotherm model was found to be high than another three adsorption isotherm models, this results show that the isotherm fits better at 303K than the other higher temperatures and it has been reported by many researchers[79]. Therefore, the adsorption process of an ethanolic extract of PQ leaves follows the Langmuir isotherm model. The regression co-efficient (R^2) values are given in Table 11. The K_{ads} values are high at 303k for PQ-Zn^{2+} system and reduce with the increasing temperatures, indicating that the inhibitor is more strongly adsorbed on the metal surface of low temperature than at higher temperatures[80]. The K_{ads} values are given in Table 2. The various isotherm plots for the adsorption of ethanolic extract of PQ leaves on the carbon steel surface are shown in Figures 9, 10, 11 and 12.

Table 11. R^2 values of various isotherms for303K

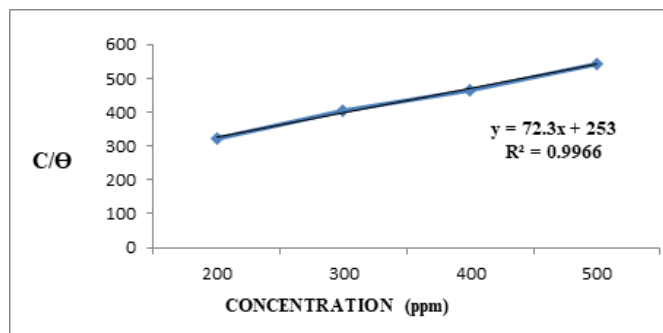| various isotherm of combined inhibitor system	R^2
Langmuir	0.997
Flory-Huggins	0.928
El-Awady	0.992
Temkin	0.989

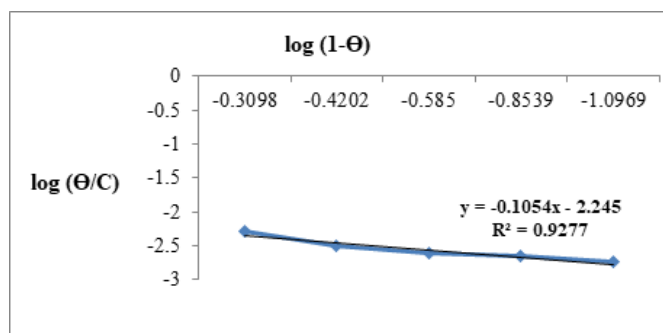**Fig 9.** Langmuir adsorption isotherm of PQ inhibitor system at 303K

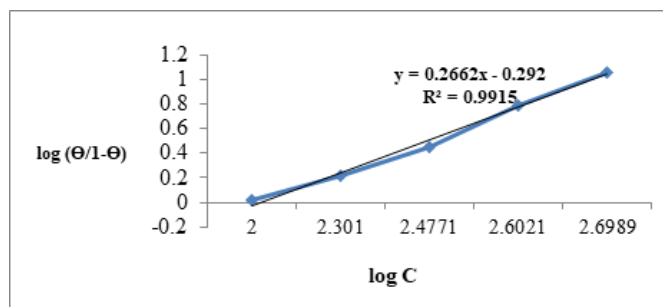**Fig 10.** Flory – Huggins Adsorption Isotherm of PQ inhibitor system at 303K

Fig 11. El-Awady Adsorption Isotherm of PQ inhibitor system at 303K
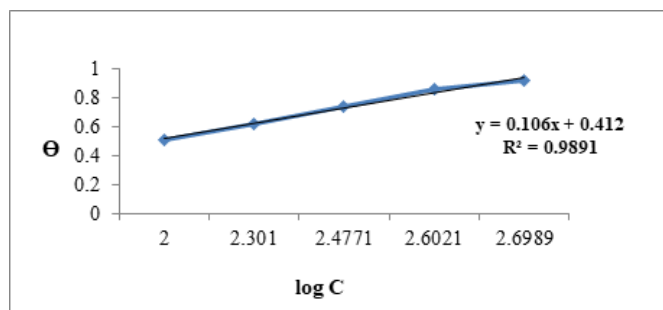

Fig 12. Temkin Adsorption Isotherm of PQ inhibitor system at 303K

4 Conclusion

The formulation consisting of 500ppm of PQ and 30ppm of Zn^{2+} system indicates 92% inhibition efficiency by using the weight-loss method. The synergism parameters confirm the existence of a synergistic effect between PQ and Zn^{2+} ion. The F-Test confirms the effects of 10ppm and 20ppm of Zn^{2+} on inhibition efficiencies of different concentration of PQ is not statistically significant and 30ppm of Zn^{2+} on the inhibition efficiencies of different concentration of PQ is statistically significant. The Tafel slopes indicate that the PQ–Zn^{2+} system behaves as a mixed type inhibitor. AC impedance spectra confirm the formation of a protective layer on the carbon steel surface. The values of positive enthalpy changes show that the corrosion process occurs as endothermic reaction. The ΔG_{ads} values are negative in sign and range from -16.1 to -18.0KJ/mol, the free energy of adsorption indicated that the corrosion inhibition take place by spontaneous physical adsorption of an ethanolic extract of PQ leaves on the carbon steel surface. The regression coefficient (R^2) values indicate that the adsorption of an ethanolic extract of *Portulaca quadrifida* leaves follows the Langmuir adsorption isotherm model. The Kads values indicate that the strongly adsorbed of an ethanolic extract of PQ leaves on the carbon steel surface. The microscopic studies including SEM, EDX, and AFM have indicated the presence of smooth surface in case of inhibited carbon steel when compared to the unhibited systems. The future work should be carried out in different metals with various corrosion mediums by using different methods, due to the ethanolic extract of PQ leaves is biodegradable, cheap, eco-friendly, and effective in well-water systems as a corrosion inhibition on the metal surface.

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