

# To Investigate the Inhibitive Action of Portulaca Quadrifida Extract as Green Corrosion Inhibitor on Carbon Steel in an Aqueous Environment

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**Abstract:** The corrosion inhibition efficiency of Portulaca Quadrifida Extract (PQE) in controlling corrosion of carbon steel immersed in sea water for one day in the presence and absence of  $Zn^{2+}$  has been studied by weight loss method. The formulation consisting of 3mL of PQE and 50 ppm of  $Zn^{2+}$  gives 97% inhibition efficiency. The synergistic effect exists between PQE and  $Zn^{2+}$  ion has been confirmed by statistical studies of Synergism parameter (S) and F-test. Polarization study suggests that PQE -  $Zn^{2+}$  system function as mixed type inhibitor. AC impedance studies confirms that the presence of protective film on the metal surface. FT-IR spectra indicate that protective film consisting of  $Fe^{2+}$  - PQE complex and  $Zn(OH)_2$ .

**Keywords:** inhibition efficiency, Synergism parameter, protective film, FT-IR spectra

## I. INTRODUCTION

Corrosion is degradation of materials properties due to interactions with their environments. Chloride, sulphate and nitrate ions in aqueous media are aggressive and accelerate corrosion [1]. Green corrosion inhibitors are cheap, biodegradable and do not contain heavy metals or other toxic substances [2]. Several investigations have been reported using plant extracts of Henna [3], Piperaceae [4], Ochrosiaopposit ifolia [5], Citrus aurantiifolia [6], Jasminumnudiflorum Lindl. [7], Andro graphis paniculata [8], Azadirachta Indica [9], Fig leaves [10], Clematis gouriana [11], Nicotianatabacum [12], Polyalthia Longifolia [13], Aloes leaves [14], Clerodendrum hlomidis [15], Morinda Tinctoria [16], Arganiaspinosa [17], Ochrosiaoppositi folia[18], Pisidiumgujava [19], Allium sativum[20], Medicago sativa [21] as eco-friendly corrosion inhibitor for metals in different media by several authors. Rajendran, et al., have investigated the inhibitive property of an aqueous extract of Rhizome powder in controlling corrosion of carbon steel in an aqueous solution containing 60ppm of chloride ion [22]. In the present work, the inhibition efficiency of Portulaca Quadrifida Extract (PQE) as inhibitor for the corrosion of carbon steel in aqueous solution containing 60 ppm of  $Cl^-$  is discussed on the basis of weight loss method, potentiodynamic polarization study, electrochemical technique.

## II. MATERIALS AND METHODS

### A. Preparation of the specimen

Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron were polished to a mirror finish and degreased with acetone and used for the weight loss method and surface examination studies

### B. Preparation of Portulaca Quadrifida Extract (PQE)

An aqueous extract of Portulaca Quadrifida Extract (PQE) was prepared by grinding 10g of Portulaca Quadrifida, with distilled water, filtering the suspending impurities, and making up to 100 ml. The extract was used as corrosion inhibitor in the present study.

### C. Weight-loss method

Carbon steel specimens were immersed in an aqueous solution containing 60 ppm  $Cl^-$  in various concentrations of the inhibitor Portulaca Quadrifida Extract (PQE) in the absence and presence of  $Zn^{2+}$  for one day. The weights of the specimens before and after

immersion were determined using a Digital Balance (Model AUY 220 SHIMADZU). The corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = \frac{W_1 - W_2}{W_1}$$

Where  $W_1$  is the weight loss value in the absence of inhibitor and  $W_2$  is the weight loss value in the presence of inhibitor.

#### D. Analysis of Variance (F-Test)

F-Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [23, 24]. If F-value is above 5.32 for 1,8 degrees of freedom, it was proved to be at statistically significant. If it is below the value of 5.32 for 1,8 degrees of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

#### E. Potentiodynamic Polarization

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

#### F. AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part ( $Z'$ ) and imaginary part ( $Z''$ ) of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance ( $R_t$ ) and the double layer capacitance ( $C_{dl}$ ) were calculated. AC impedance spectra were recorded with initial  $E(v) = 0$ , high frequency (Hz) =  $1 \times 10^5$ , low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

#### G. Fourier transform infrared spectra

The carbon steel specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

### III. RESULT AND DISSCUSION

#### A. Analysis of results of weight loss study

The calculated Inhibition efficiencies (IE) and corresponding corrosion rates (CR) of an Portulaca Quadrifida Extract (PQE) on the corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$  in the presence and absence of  $Zn^{2+}$  has been evaluated by weight loss method.

Table 1: Corrosion rates (CR) and inhibition efficiency of carbon steel immersed in an aqueous solution in the absence and presence of inhibitors

S.No	Cl <sup>-</sup> (ppm)	PQE (mL)	Zn <sup>2+</sup> (0 ppm)		Zn <sup>2+</sup> (25 ppm)		Zn <sup>2+</sup> (50 ppm)	
			IE%	CR (mmpy)	IE%	CR (mmpy)	IE%	CR (mmpy)
1	60	0	-	0.5084	16	0.4262	21	0.4013
2	60	1	65	0.1779	72	0.1420	77	0.1167
3	60	2	73	0.1370	78	0.1108	89	0.0556
4	60	3	79	0.1054	85	0.0671	97	0.0151
5	60	4	76	0.1218	82	0.0917	94	0.0303
6	60	5	70	0.1522	75	0.1269	83	0.0864

Inhibitors : Portulaca Quadrifida (PQE) +  $Zn^{2+}$

Period of immersion : 1 day

Results from the above table show that when the carbon steel is immersed in aqueous solution containing 60 ppm of  $\text{Cl}^-$  3mL of Portulaca Quadrifida Extract (PQE) only shows 65% inhibition efficiency (IE) (in the absence of  $\text{Zn}^{2+}$ ). This inhibition efficiency is found to be increased in the presence of  $\text{Zn}^{2+}$  ions. When  $\text{Zn}^{2+}$  is added IE also increases and gives maximum 97 % IE at 3mL of PQE and 50 ppm of  $\text{Zn}^{2+}$  this shows that synergistic effect exists between  $\text{Zn}^{2+}$  and the active principles present in PQE. For example, 50 ppm of  $\text{Zn}^{2+}$  has only 21 % of IE; 3mL of PQE has 65 percent IE. Interestingly their combination has High IE, namely, 97%. Therefore the mixture of inhibitors shows better IE than individual inhibitors.

When the concentration of PQE-  $\text{Zn}^{2+}$  increases from 25 ppm to 50 ppm the IE slightly increases. This is due to the fact that, when the concentration of  $\text{Zn}^{2+}$  increases, the  $\text{Zn}^{2+}$ -PQE complex formed in the bulk of the solution. After increasing concentration of PQE the IE decreases. This may be due to the fact that, when the concentration of PQE increases, the  $\text{Zn}^{2+}$ -PQE complex formed is precipitated in the bulk of solution. These similar observation was made with Hibiscus Rosa-Sinensis Al at pH 12 [25], Euphorbia [26].

*B. Influence of immersion period on IE of PQE -  $\text{Zn}^{2+}$  system*

The influence of immersion period (IP) on the IE of 3 mL of PQE and 50 ppm of  $\text{Zn}^{2+}$  system is given in Table 2. It is found that as the Immersion Period increases the IE decreases. This is due to the fact that as the Immersion Period increases, the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions present in the well water. There is a competition between the formation of  $\text{FeCl}_2$  (and also  $\text{FeCl}_3$ ) and  $\text{Fe}^{2+}$ -PQE complex on the anodic sites of the metal surface. It appears that the formation of iron chlorides is more favoured than the formation of  $\text{Fe}^{2+}$ -PQE complex. Moreover, the  $\text{Fe}^{2+}$ -PQE complex film formed on the metal surface is converted into iron chloride which goes into solution and, the IE decreases as the Immersion Period increases. Similar observations were shown in Phyllanthus amarus extract [27],  $\text{Fe}^{2+}$ -curcumin system [28].

Table 2:

Influence of immersion period (IP) on the IE of PQE -  $\text{Zn}^{2+}$  system  
 Inhibitor system: PQE -  $\text{Zn}^{2+}$  Immersion period: 1 day

Immersion period (days)	Corrosion Rate (CR) in the absence of the inhibitor (mmpy)	Corrosion Rate (CR) in the presence of the inhibitor PQE (3mL) + $\text{Zn}^{2+}$ (50 ppm) (mmpy)	Inhibition Efficiency (IE%)
1	0.5084	0.0151	97
3	0.5915	0.1315	78
5	0.6720	0.3951	56
7	0.7070	0.3946	44

*C. Synergism parameter ( $S_1$ ):*

Table 3: Synergism Parameters derived from inhibition efficiencies of PQE-  $\text{Zn}^{2+}$  (50 ppm) system for one day:

PQE (mL)	$\text{Zn}^{2+}$ (ppm)	$I_1$	$I_2$	$I_{1+2}$	$S_1$	IE%
1	25	0.65	0.16	0.72	1.0500	72
2	25	0.73	0.16	0.78	1.0304	78
3	25	0.79	0.16	0.85	1.1760	85
4	25	0.76	0.16	0.82	1.1200	82
5	25	0.70	0.16	0.75	1.0080	76

Table 4: Synergism Parameters derived from inhibition efficiencies of PQE- Zn<sup>2+</sup> (50 ppm) system for one day:

PQE (mL)	Zn <sup>2+</sup> (ppm)	I <sub>1</sub>	I <sub>2</sub>	I <sub>1+2</sub>	S <sub>I</sub>	IE%
1	50	0.65	0.21	0.77	1.2021	77
2	50	0.73	0.21	0.89	1.9390	89
3	50	0.79	0.21	0.97	5.5300	97
4	50	0.76	0.21	0.94	3.1600	94
5	50	0.70	0.21	0.83	1.3941	83

Synergism Parameter (S<sub>I</sub>) has been calculated to know the synergistic effect existing between two inhibitors [29, 30]. The values of S<sub>I</sub> > 1 suggest a synergistic effect. S<sub>I</sub> approaches 1 when no interaction exists between the inhibitor compounds. In case of S<sub>I</sub> < 1, the negative interaction of inhibitors prevails (i.e., corrosion rate increases).

Synergism parameter is calculated using the following relation.

$$S_I = \frac{1 - I_{1+2}}{1 - I_1 - I_2}$$

Where, I<sub>1</sub> is the surface coverage of inhibitor (PQE), I<sub>2</sub> is the surface coverage of inhibitor (Zn<sup>2+</sup>) and I<sub>1+2</sub> is the combined surface coverage of inhibitors (PQE) and (Zn<sup>2+</sup>). The calculated synergism parameter values for Portulaca Quadrifida Extract (PQE) and Zn<sup>2+</sup> synergism are given in the table 3 and 4.

Synergism Parameter (S<sub>I</sub>) for the formulation consisting of 3mL of PQE and 50 ppm of Zn<sup>2+</sup> ions are 5.5300 which is greater than one. This shows that the synergistic effect exists between PQE and Zn<sup>2+</sup>.

*D. Analysis of F-values (analysis of variance ANOVA):*

To investigate whether, the influence of Zn<sup>2+</sup> on the inhibition efficiencies of ANSA is statistically significant, F-test was carried out [31]. The results are given in Table 6. The results of Analysis of variance (ANOVA) shows the influence of 25 ppm and 50 ppm of Zn<sup>2+</sup> on the inhibition efficiencies of 1mL, 2mL, 3mL, 4mL, 5mL, of PQE.

Table 6: Distribution of F – value between the inhibition efficiencies of various concentrations of PQE (0 ppm of Zn<sup>2+</sup>) and the inhibition efficiencies of PQE in the presence of 25 and 50 ppm of Zn<sup>2+</sup>

Zn <sup>2+</sup> (ppm)	Source of Variance	Sum of Squares	Degree of freedom	Mean square	F-value	Level of Significance of F
25	Between	84	1	84	3.700	P> 0.05
	Within	227	10	22.7		
50	Between	592	1	592	15.497	P> 0.05
	Within	382	10	38.2		

The obtained F-value 3.700 for 25 ppm Zn<sup>2+</sup>, was not statistically significant, since it was less than the critical F-value 4.96 for 1, 10 degrees of freedom at 0.05 level of significance. Therefore, it was concluded that the influence of 25 ppm Zn<sup>2+</sup> on the inhibition efficiencies of various concentrations of PQE was not statistically significant.

The obtained F-value 15.497 for 50 ppm Zn<sup>2+</sup> was statistically significant, since it was greater than the critical F-value 4.96 for 1, 10 degrees of freedom at 0.05 level of significance. Therefore, it was concluded that the influence of 50 ppm Zn<sup>2+</sup> on the inhibition efficiencies of various concentrations of PQE was statistically significant.

*E. Analysis of polarization curves*

Polarization study has been used to detect the formation of protective film on the metal surface [32, 33]. When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current ( $I_{corr}$ ) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Fig.1 The corrosion parameters namely, corrosion potential ( $E_{corr}$ ), Tafel slopes ( $b_c$ =cathodic;  $b_a$ =anodic), linear polarization resistance (LPR) and corrosion current ( $I_{corr}$ ) are given in Table 7.

When carbon steel is immersed in an aqueous solution containing 60 ppm of  $Cl^-$ , the corrosion potential is -522 mV Vs SCE. The formulation consisting of 3mL of PQE + 50 ppm  $Zn^{2+}$  shifts the corrosion potential to -500 mV Vs SCE. It shows that the corrosion potential is shifted to less negative side.

The formulation consisting of PQE and  $Zn^{2+}$  shifts the anodic slopes and cathodic slopes (177.6 mV/dec and 179.22 mV/dec ) almost equally controls both anodic and cathodic reaction . This suggests that the PQE- $Zn^{2+}$  formulation performs as a mixed type inhibitor.

The corrosion current value and LPR value for in an aqueous solution containing 60 ppm of  $Cl^-$   $5.375 \times 10^{-6} A/cm^2$  and  $2755.8 \Omega cm^2$ . In the presence of the inhibitors, the corrosion current value has decreased to  $3.576 \times 10^{-6} A/cm^2$  and the LPR value has increased to  $7951.5 \Omega cm^2$ . When a protective film is formed on the metal surface, LPR value increases and corrosion current value decreases. It can be said that the inhibition of corrosion of carbon steel in an aqueous solution containing 60 ppm of  $Cl^-$  containing 3mL of PQE and 50 ppm  $Zn^{2+}$  of by PQE- $Zn^{2+}$  system

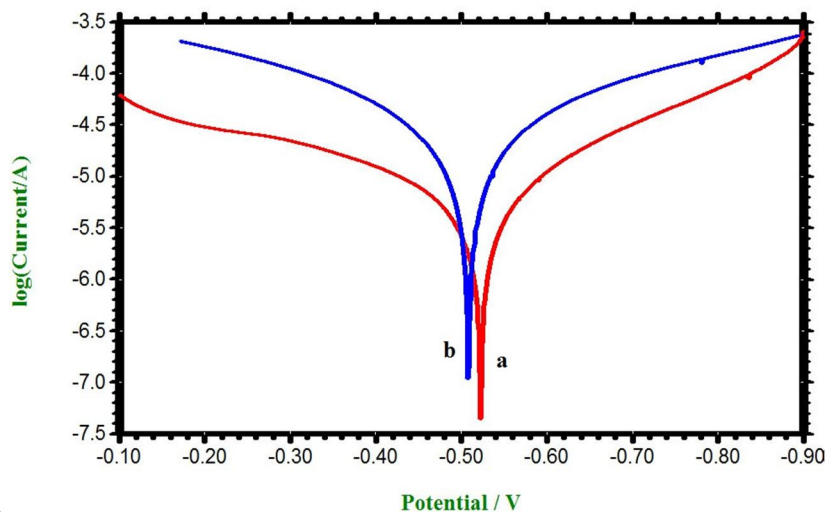


Figure 1. Polarization curves of carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$

a)  $Cl^-$  60 ppm solution

b) 3mL of PQE + 50 ppm of  $Zn^{2+}$  +  $Cl^-$  60 ppm

Table 7. Corrosion parameters of carbon steel immersed in  $Cl^-$  60 ppm solution in the presence and absence of inhibitor obtained by polarization method:

Concentration		Tafel Parameters				
PQE (mL)	$Zn^{2+}$ (ppm)	$E_{corr}$ (mV vs SCE)	$I_{corr}$ ( $A/cm^2$ )	$b_a$ (mV/dec)	$b_c$ (mV/dec)	LPR ( $\Omega cm^2$ )
0	0	-522	$5.375 \times 10^{-6}$	236.29	198.30	2755.8
3	50	-500	$3.576 \times 10^{-6}$	177.6	179.22	7951.5

*F. Analysis of AC impedance spectra:*

Nyquist representations of carbon steel in well water in the absence and presence of the inhibitor system are shown in Fig.4.3 AC impedance spectra have been used to detect the formation of film on the metal surface [34,35]. If a protective film is formed, the charge transfer resistance ( $R_{ct}$ ) increases and double layer capacitance ( $C_{dl}$ ) value decreases. It is observed from the plots that the impedance response of carbon steel was significantly changed after addition of the inhibitors. The impedance diagrams obtained

almost have a semicircular appearance. This indicates that the corrosion of carbon steel in aqueous solution is mainly controlled by a charge transfer process. The deviation from the perfect semicircle shape is due to the frequency dispersion of interfacial impedance. This anomalous behavior is because of the non-homogeneity of the metal surface arising from surface roughness or interfacial phenomena. The impedance parameters, namely charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) are given in Table 8.

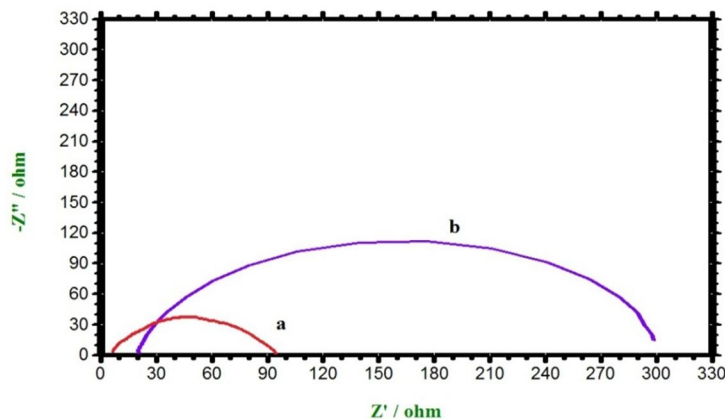


Figure 2. AC impedance of carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$ :

a)  $Cl^-$  60 ppm solution

b) PQE (3mL) + 50 ppm of  $Zn^{2+}$  +  $Cl^-$  60 ppm

When carbon steel is immersed in an aqueous solution containing 60 ppm of  $Cl^-$ ,  $R_{ct}$  value is  $94.4 \Omega cm^2$  and  $C_{dl}$  value is  $2.3684 \times 10^{-4} \mu F/cm^2$ . When  $Zn^{2+}$  and PQE are added to seawater,  $R_{ct}$  value increases from  $94.4 \Omega cm^2$  to  $280.8 \Omega cm^2$  and the  $C_{dl}$  value decreases from  $2.3684 \times 10^{-4} \mu F/cm^2$  to  $1.6452 \times 10^{-4} \mu F/cm^2$ . These results lead to the conclusion that a protective film is formed on the metal surface. If the inhibition efficiency values obtained from weight loss, polarization and EIS studies are compared, differences are observed. It is suggested that the inhibition efficiency values obtained from various methods may not be strictly comparable when the immersion times used in these methods are not the same [36].

Table 8. Corrosion parameters of carbon steel immersed in  $Cl^-$  60 ppm solution in the presence and absence of inhibitor obtained by AC impedance spectra:

PQE (3mL)	$Zn^{2+}$ (ppm)	$R_{ct}$ ( $\Omega cm^2$ )	$C_{dl}$ ( $\mu F/cm^2$ )
0	0	94.4	$2.3684 \times 10^{-4}$
3	50	280.8	$1.6452 \times 10^{-4}$

### G. Analysis of FTIR spectra

FTIR spectra have been used to analyze the protective film formed on metal surface [37, 38]. A few drops of an aqueous extract of Portulaca Quadrifida was dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown Fig. 4 a. The C=O stretching frequency appears at  $1632 cm^{-1}$ . The -OH stretching frequency appears at  $3421 cm^{-1}$ . The asymmetric C-O-C stretching frequency appears at  $1237 cm^{-1}$ . The symmetric C-O-C stretching frequency appears at  $1067 cm^{-1}$ . The FTIR spectrum of complex prepared by mixing Portulaca Qudrifida Extract and  $Fe^{2+}$  is shown in Fig 4.b. The C=O stretching frequency shifts from  $1632 cm^{-1}$  to  $1629 cm^{-1}$ . The -OH stretching frequency shifts from  $3391 cm^{-1}$  to  $3377 cm^{-1}$ . The asymmetric C-O-C stretching frequency shifts from  $1237 cm^{-1}$  to  $1233 cm^{-1}$ . The symmetric C-O-C stretching frequency shifts from  $1067 cm^{-1}$  to  $1063 cm^{-1}$ . These frequency shifts show the formation of complex between  $Fe^{2+}$  and PQE. These shifts confirm that the formation of  $Fe^{2+}$  - PQE complex on the anodic sites of the metal surface. The peak at  $1374 cm^{-1}$  is due to  $Zn(OH)_2$  formed on the cathodic sites of the metal surface [39, 40]. The major active compound in Portulaca Quadrifida Extract (PQE) is Kaempferol (IUPAC: 3,5,7- Trihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one) with structure in figure 3.

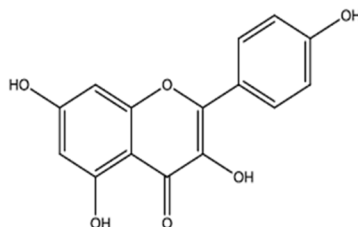


Figure 3: Structure of Kaempferol  
(IUPAC: 3,5,7- Trihydroxy-2-(4-hydroxyphenyl)-4H-chromen4-one)

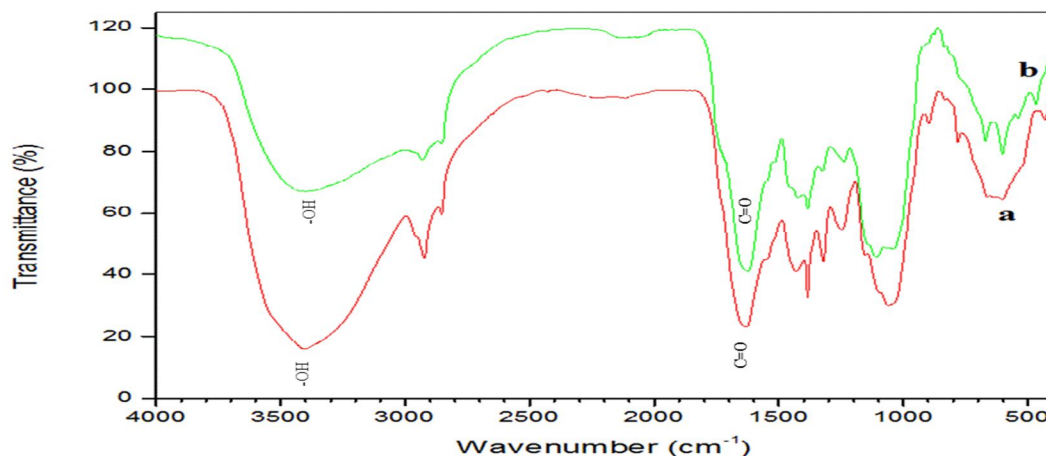


Fig.4. FT-IR spectra of  
a) pure Portulaca Quadrifida Extract (PQE)  
b) protective film formed on the surface of the metal immersed in an aqueous solution containing 3mL of Portulaca Quadrifida Extract (PQE) and 50 ppm of  $Zn^{2+}$ .

#### IV. CONCLUSIONS

The present study leads to the following conclusions.

- A. The formulation consisting of 3mL of Portulaca Quadrifida Extract (PQE) and 50 ppm of  $Zn^{2+}$  offers 97% inhibition efficiency to carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$ .
- B. The synergism parameter ( $S_I$ ) and F-test confirms that synergistic effect exists between the Portulaca Quadrifida Extract (PQE) -  $Zn^{2+}$  system in controlling the corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$  in the absence and presence of  $Zn^{2+}$ .
- C. Polarization study reveals that this system formulation acts as a mixed type of inhibitor.
- D. AC impedance spectra reveal that a protective film is formed on the metal surface.
- E. The FTIR spectra reveal that the protecting film consists of  $Fe^{2+}$ - PQE (active ingredient) complex.

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