PortulacaQuadrifida Extract (PQE) as Green Corrosion Inhibitor for Carbon Steel in Well Water

P. Thirupathi[1], S.K. Selvaraj[2], A. John Amalraj[1] & B.R. Venkatraman[1]
[1]PG and Research Department of Chemistry, Periyar E.V.R College, Tiruchirappalli – 620023
[2]PG and Research Department of Chemistry, G.T.N Arts.College, Dindigul - 624005

Received: August 29, 2018 Accepted: October 15, 2018

ABSTRACT *The corrosion inhibition efficiency of PortulacaQuadrifida Extract (PQE) in controlling corrosion of carbon steel immersed in well water for one day in the presence and absence of Zn^{2+} has been studied by weightloss method. The formulation consisting of 3mL of PQE and 50ppm of Zn^{2+} gives 98% inhibition efficiency. Polarization study suggests that PQE-Zn^{2+} system function as mixed type inhibitor. A Cimpedance studies confirms that the presence of protective film on the metal surface. FT-IR spectra indicate that protective film consisting of Fe^{2+}-PQE complexand Zn(OH)2.*

Keywords: *PortulacaQuadrifida Extract, Protective film, Polarization study, FT-IR.*

1. INTRODUCTION

Extracts andconstituents of plants have been used by several corrosion practitioners to mitigate the menace of corrosion. Naturally occurring substances are cheap and renewable, biodegradable and do not contain heavy metals or other toxic chemicals ,eco-friendly and hence ecologically acceptable [1]. Selvaraj et al., investigated the inhibitive action of Pisonia Alba as corrosion inhibitor for carbon steel in HCl solution [2]. 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 60 ppm of chloride ion [3]. Sathiyabama et al and co-workers have reported an aqueous extract of banana peel as corrosion inhibitor for carbon steel in sea water [4]. Sakthivel et al., have been studied phyllathusniruri as green corrosion inhibitors for carbon steel in well water [5].

The present work is undertaken:

1. To evaluate the inhibition efficiency (IE) of PQE-Zn^{2+} system in controlling corrosion of carbon steel immersed in well water by weight loss method.
2. To investigate the type of inhibitors and its protective formation on the metal surface analysed by polarization study and AC impedance study.
3. To analyse the nature of protective film by FTIR spectra.
4. To propose the mechanism of corrosion inhibition based on the above results

2.MATERIALS AND METHODS

2.1.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 trichloroethylene and used for the weight loss method and surface examination studies.

2.2.Preparation of plant extract

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

Table.1: Main constituents of PortulacaQuadrifida Extract (PQE)are shown below:

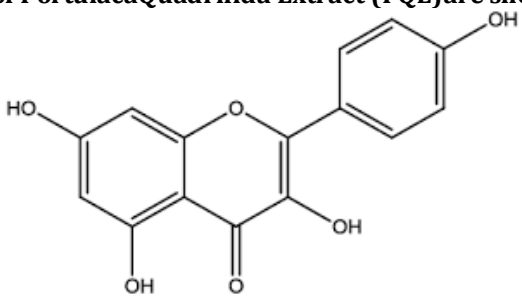

Figure 1: Structure of 3,5,7- Trihydroxy-2-(4-hydroxyphenyl)-4H-chromen4-one

2.3.Weight-loss method

Carbon steel specimens were immersed in 100 ml of well water in containing various concentrations of the inhibitor PortulacaQuadrifida 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

$$IE = 100\ [1-(W_2/W_1)]\ \%$$

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.

2.4. Potentiodynamic Polarization

Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided withiR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr), Tafel slopes anodic = ba and cathodic = bc were calculated and polarization study was done. The scan rate (V/S) was 0.01. Hold time at (Efcs) was zero and quiet time (s) was two.

2.5. 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 (Rt) and the double layer capacitance (C_{dl}) were calculated. AC impedance spectra were recorded with initial E(v) = 0, high frequency (Hz) = 1x105, low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

2.6. Surface examination study

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 various surface analysis techniques.

2.6.1.Fourier transform infrared spectra

These spectra were recorded in a 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.

3. RESULTS AND DISCUSSION:

3.1. Analysisofresultsofweight-lossstudy

The corrosion rate (CR) andInhibition Efficiency (IE) of carbon steel immersed in well water in the absence and presence of inhibitor systems are given in Tables 1.

Table 1: Corrosion rates of carbon steel and inhibition efficiencies of various concentrations of PortulacaQuadrifida Extract (PQE) in well water

PQE (mL)	Zn^{2+}		Zn^{2+}		Zn^{2+}	
	IE %	CR	IE %	CR	IE %	CR
0	-	0.8601	14	0.6792	21	0.7391
1	52	0.4127	67	0.2833	72	0.2403
2	65	0.3010	73	0.2314	84	0.1370
3	72	0.2403	85	0.1285	98	0.0168
4	62	0.3267	80	0.1720	87	0.1117
5	58	0.3609	70	0.2571	79	0.1804

It is seen from table 1 that PQE alone shows 72 % . When the concentration of Zn^{2+} increases from 25 ppm to 50 ppm the IE is found to be increased. The formulation consisting of 3mL of PQE and 50 ppm of Zn^{2+} gives maximum IE 98%. When the concentration of PQE was increased the IE decreased. This due to the fact that when higher concentrations of PQE are added the protective film (Fe^{2+}-PQE Complex) formed on the metal surface goes into solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken. Hence the IE decreases, similar observation was made with Hibiscus Rosa-Sinensis Al [6], Euphorbia [7], Henna [8], Banana Peel [4].

3.2. Analysis of Polarizationstudy:

The polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in figure 2. The corrosion parameters are given in Table 2.

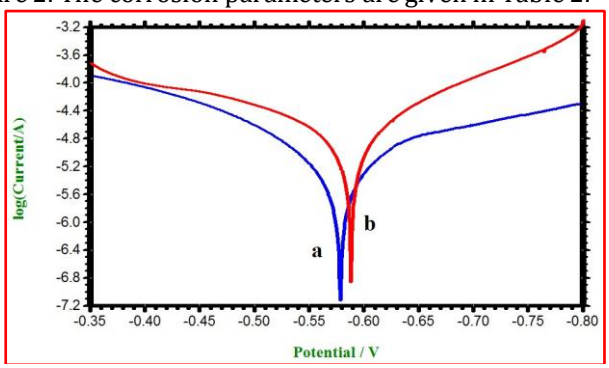

Fig. 2. Polarization curves of carbon steel immersed in
(a) well water
(b) 3mL PQE + 50 ppm of Zn^{2+} + well water

Table 2: Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by polarization method:

Concentration		Tafel Parameters					IE (%)
PQE (mL)	Zn^{2+} (ppm)	E_{corr} (mV vs SCE)	I_{corr} (A/cm^2)	b_a (mV/dec)	b_c (mV/dec)	LPR (Ω cm^2)	
0	0	-580	5.5431×10^{-5}	116.23	110.88	963	88
3	50	-590	0.6897×10^{-5}	185.89	180.32	3671	

When carbon steel is immersed in well water, the corrosion potential is-580mV vsSCE. The formulation consisting of 3 mL of PQE and 50 ppm of Zn^{2+}shifts the corrosion potential is-590mVvsSCE. The formulation consisting of PQE and Zn^{2+} shifts the anodic slopes and cathodic slopes (185.89 mV/dec and 180.32 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 (I_{corr}) and LPR (Ωcm^2) value for well water 5.5431×10^{-5} A/cm^2 and 3130 Ωcm^2. For the formulation of PQE (3 mL)and Zn^{2+}(50ppm), the corrosion current value has decreased to 0.6897×10^{-5} A/cm^2 and the LPR value has increased to 3671Ωcm^2. This indicates that aprotective film is formed on the metal surface. When a protective film is formed on the metal surface LPR value increases and corrosion current value decreases [9].

3.3. Analysis of AC impedance Study

The AC impedance spectra of carbon steel immersed in various test solution are shown in Figure 3. The charge transfer resistance(R_{ct}) and double layer capacitance (C_{dl}) are given in Table 3. When carbon steel is immersed in well water, the R_{ct} value is 391 Ω cm^2 and C_{dl} value is $1.3137 \times 10^{-6}\mu F/cm^2$. In the presence of inhibitor system (3 mL of PQE and 50 ppm of Zn^{2+}), the R_{ct} value increases from391Ω cm^2 to 3018 Ω cm^2 and the C_{dl} value decreases from$1.3137 \times 10^{-6}\mu F/cm^2$ to $0.0253\times 10^{-6}\mu F/cm^2$. This confirms the formation of a protective film on the metal surface [10].

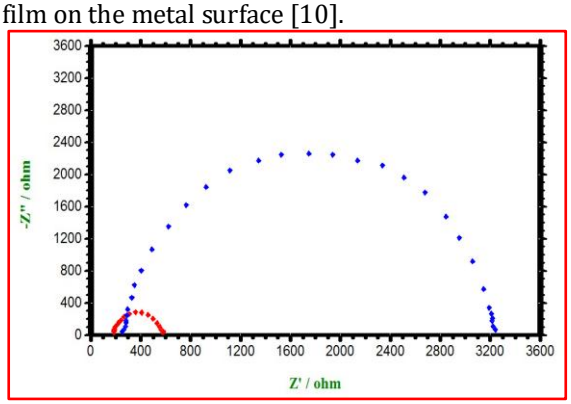

Fig. 3. AC impedance of carbon steel immersed in well water
a) well water
b) 3mL PQE + 50 ppm of Zn^{2+} + well water

Table 3: Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by AC impedance spectra:

PQE (mL)	Zn^{2+} (ppm)	R_{ct} (Ω cm^2)	C_{dl} ($\mu F/cm^2$)	IE (%)
0	0	391	1.3137×10^{-6}	
3	50	3018	0.0253×10^{-6}	87

3.4. Analysis of FTIR spectra

FTIR spectra have been used to analyze the protective film formed on metal surface. A few drops of an aqueous extract of PortulacaQuadrifidawere dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown in Fig.3 a. The C=O stretching frequency appears at 1680 cm^{-1}. The OH stretching frequency appears at 3429 cm^{-1}. The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing well water, 3 mL of PQE and 50 ppm of $Zn^{2+}$is shown in Fig.3 b. It is found that the–OH stretching frequency has shifted from 3429 cm^{-1} to 3415 cm^{-1}. The C=O stretching frequency has shifted from 1680 cm^{-1} to 1678 cm^{-1}.These shifts confirm that the formation of Fe^{2+} - PQE complex on the anodic sites of the metal surface.The peak appears at 503 cm^{-1} could be attributed to the Zn-O stretching frequency.The FT-IR results indicate the formation of a protective film on themetal surface and may consists of Fe^{2+}-PQE complex and $Zn(OH)_2$[11,12].

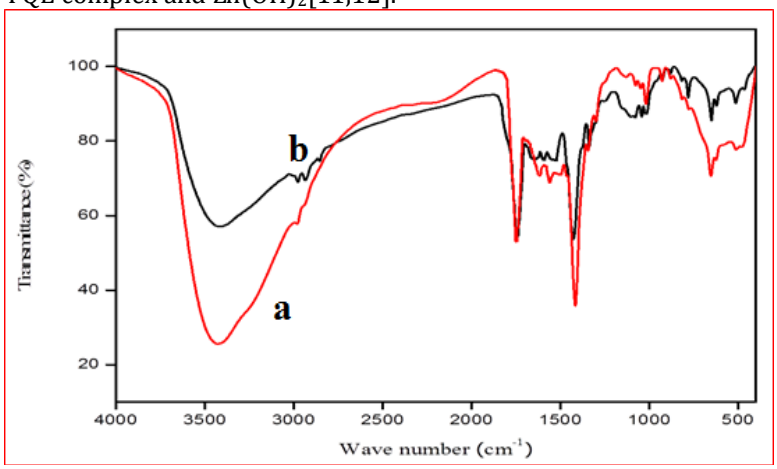

Fig.4. FT-IR spectra of
a) pure PQE
b) protective film formed on the metal surface immersed in well water containing 3mL PQE + 50 ppm of Zn^{2+}

3.5. Mechanism of corrosion inhibition

The Weight – loss study showed that the 3 mL of PQE and 50 ppm of Zn^{2+}offer excellent inhibition efficiency. A corrosion inhibition mechanism proposed based on Weight – loss study ,AC impedance, polarization study and FTIR studies[13].

When well water consisting of 3 mL of PQE and 50 ppm of Zn^{2+} are prepared, there is a formation of Zn^{2+}-PQE complexin solution.

When the carbon steel introduced in this solution, there is diffusion of zinc complexes move towards the carbon steel surface.

On the carbon steel surface, zinc complex is converted into iron complex on the anodic site.

$$Zn^{2+}\text{-PQE} \longrightarrow Fe^{2+}\text{-PQE}$$

The released Zn^{2+} combined with OH- to form $Zn(OH)_2$ on the cathodic Sites.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

Thus, protective film consists of Fe^{2+}-PQE complex and $Zn(OH)_2$.

4. CONCLUSION

The present study leads to the following conclusions:

1. Weight loss study reveals that the formulation consisting of 3ml of PQE and 50 ppm of Zn^{2+} has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in well water.

2. Polarization study reveals that Zn^{2+}- PQEsystem functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to equal extents.
3. AC impedence spectra reveal that a protective film is formed on the metal surface.
4. FTIR spectra show that the protective film consists of Fe^{2+}- PQE complex and $Zn(OH)_2$.

REFERENCE:

1. Dar M.A., Ind. Lubr. Tribol, 2011; 63: 227.
2. S. K. Selvaraj, IJRASET, ISSN: 2321-9653, Volume 6 Issue II, February 2018
3. S.Rajenderan, S.Shanmugapriya, T.Rajalakshmi, A.J.AmalRaj, Corrosion 61(7), (2005), pp.685-692.
4. M.Sangeetha, S.Rajendran, J.Sathiyabama and P.Prabhakar, J. Nat. Prod. Plant Resour., 2012, ISSN : 2231 – 31842 (5):601-610,
5. Sakthivel, K. Karthik Kumar, S. K. Selvaraj, A. John Amalraj, international research journal of india, ISSN 2454-8707, volume II, issue VIII, Apr-2017.
6. S.Rajendran, J.Jeyasundari, P.Usha, J.A.Selvi, B.Narayanasamy, A.P.P.Regis, P.Rengan, PortugaliaeElectrochemicaActa (2009) 27 (2): 153-164.
7. P.K. Kasthuri, A. Arulanantham, Asian Journal of Chemistry (2010) 22(1): 430-434.
8. S. Rajendran, M. Agasta, R. Bama Devi, B. Shyamala Devi, K. Rjam, J. Jeyasundari, ZastitaMaterijala (2009)50 (2): 77-84.
9. P.K. Kasthuri, A. Arulanantham, Asian Journal of Chemistry (2010) 22(1): 430-434.
10. Apparao B.V., Christina K., Indian J. Chem. Technol. 13 (2006) 275.
11. I.Sekine, Y.Hirakawa, Corrosion. 42, (1986), 272.
12. M. Manivannan, S. Rajendran, Research Journal of chem. Sciences. 1, (2011), 42.
13. S.AgnesiaKanimozhi, S.Rajendran, Int.J.Electrochem. Sci. 4, (2009), 35