An aqueous ExtractofPisonia Alba as Eco-friendly Corrosion Inhibitor for Carbon Steel inwell 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 26, 2018 Accepted: October 14, 2018

ABSTRACT *The inhibition property of Pisonia Alba Extract (PAE) on the corrosion of carbon steel in well water was investigated using potentiondynamic, Electrochemical impedance study (EIS), weight loss technique. Weight loss study reveals that the formulation consisting of 3mL of Pisonia Alba (PSA) and 50ppm of Zn^{2+} offers 92% inhibition efficiency to carbon steel immersed in well water. The results of Polarization study reveals that this system functions as a mixed type of inhibitor. The AC impedance study reveals that a protective film formed on the metal surface. Scanning electron microscopy (SEM) observation, confirmed the existence of an inhibitor molecules on the metal surface.*

Keywords: *Pisonia Alba, inhibition efficiency, Corrosion rate, protective film*

1.INTRODUCTION:

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely [1]. The use of inhibitors is one of the best options of protecting metals against corrosion in various fields of application as acid pickling and acid descaling [2]. The inhibitors employed are varied and some have been found to be severe to health and the environment at large. Thus efforts are now directed towards formulation of modern environmentally safe inhibitors in which plant extracts have become important as eco-friendly, economical, readily available and renewable sources of effective corrosion inhibitors. Pisoniaalba (Nyctaginaceae), commonly known as Lettuce Tree, is an evergreen tree 9-12 m high found sparsely wild in the beach forests of Andaman Islands, cultivated to a small extent in India and Ceylon. The fresh leaves moistened with Eau-de-Cologne are used to subdue inflammation of a filariosis nature in the legs and other parts [3]. They are used as diuretic. The root is purgative. A survey of literature revealed that Pisonia alba is an untapped candidate for antidiabetic activity though it is extensively used in traditional healing of diabetes in Kerala (Anonymous,1969) [4]. Aqueous extract of PortulacaQuadrifida have also proved to be efficient corrosion inhibitor in low chloride media [5]. Corrosion inhibition of carbon steel in well water by Vitexnegundo extract has been studied [6]. The corrosion inhibition effects of Allium Sativum (Garlic) Extract have been reported [7]. Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of Hibiscus rosasinensis Linn has been evaluated [8]. Banana peel has been used as corrosion inhibitor for carbon steel in sea water [9].
The present study aimed at investigating the inhibitive properties of an aqueous extract of Pisonia Alba plant leaves on the corrosion of carbon steel in well water.

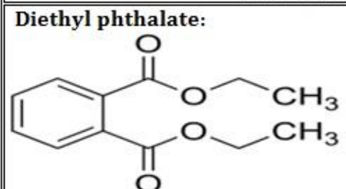
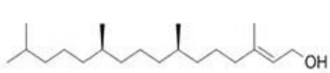
2. EXPERIMENTAL

2.1. Preparation of Specimen

Carbon steel specimen [0.0267 % S, 0.06 % P, 0.4% Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.2.Preparation of plant extract

Table.1: Main constituents of Pisonia Alba Extract (PAE)are shown below:

Pisonia Alba Extract (PAE)	
Diethyl phthalate:  Molecular formula: $C_{12}H_{14}O_4$ Molecular weight : 222.089 IUPAC: Diethyl benzene-1,2-dicarboxylate	**Phytol:**  Molecular formula: $C_{20}H_{40}O$ Molecular weight : 296.308 IUPAC: (2E,7R,11R)-3,7,11,15,-tetramethyl-2-hexadecen-1-ol

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

2.3. Corrosion Medium:

In our present study, well water chosen as corrosive media were collected from due well at Alundur, Tiruchi.

Table.2: Physiochemical parameters of well water

Parameters	Results
Appearance	Colorless
Total dissolved solids	1804 ppm
pH	7.95
Total hardness	950 ppm
Calcium	151 ppm
Magnesium	87 ppm
Iron	0.76 ppm
Conductivity	3459 Micro mho / cm
Chloride	515 ppm

2.3. Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution [10]. The inhibition efficiency (IE) was then calculated using the equation:

$$IE\ (\%) = \left[\frac{W_2 - W_1}{W_2}\right] \times 100$$

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. Polarization Study

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. The inhibition efficiency (IE) values were calculated from i^o_{corr}values using the equation[11],

$$IE\ \% = \left(\frac{i^o_{corr} - i_{corr}}{i^o_{corr}}\right) \times 100$$

Where$i^o_{corr}$and $i_{corr}$are the corrosion current densities in case of uninhibited and inhibited solutions respectively.

2.5. AC impedance spectra

The instrument used for polarization study was also used for AC impedance spectra. The cell set up was the same as that was used for polarization measurements. The real part (Z') and the imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies.AC impedance spectra were recorded with initial E(v) = 0 V, high frequency limit was 1x105 Hz, low frequency limit was 1 Hz, amplitude = 0.005 V and quiet time t_q= 2s. The values of charge transfer resistance, R_{ct}, and the double layer capacitance, C_{dl}, were calculated.

$$R_{ct} = (R_s + R_{ct}) - R_s$$

Where, $R_s$is solution resistance and

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

where $f_{max}$is maximum frequency.

2.6. Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

2.6.1. Scanning electron microscopy

The surface morphology of the formed layers on the carbon steel surface after its immersion in control solutions containing well water in the absence and in the presence of the inhibitor were carried out. After one day, the specimens were taken out, washed with distilled water and dried. The SEM photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Weight-Loss Method

Table.2: Corrosion rates (CR) of carbon steel immersed in well watercontaining in the presence and absence of inhibitor system at various concentrations of inhibitors and the inhibition efficiencies (IE) obtained by weight loss method:

Inhibitor system: Zn^{2+}- PAE **Immersion period:** one day

PAE (mL)	Zn^{2+}		Zn^{2+}		Zn^{2+}	
	IE %	CR	IE %	CR	IE %	CR
0	-	0.8601	14	0.6792	21	0.7391
1	48	0.4469	53	0.4034	62	0.3267
2	56	0.3778	63	0.3179	78	0.1889
3	64	0.3094	77	0.1973	92	0.0685
4	57	0.3697	65	0.3001	86	0.1201
5	52	0.4127	58	0.3604	73	0.2314

It is observed that when the carbon steel is immersed in well water contains 3 mL of PAE only shows 64% inhibition efficiency (IE) (in the absence of Zn^{2+}).This inhibition efficiency is found to be enhanced in the presence of Zn^{2+} ions.

When Zn^{2+} is added IE also increases and gives maximum 92 % IE at 3 mL of PAE and 50 ppm of Zn^{2+} this shows that synergistic effect exists between Zn^{2+} and the active principles present in PAE. For example, 50 ppm of Zn^{2+}has only 21 % of IE; 3mL of PAE has 64 percent IE. Interestingly their combination has High IE, namely, 92 %. Therefore the mixture of inhibitors shows better IE than individual inhibitors.

When the concentration of Zn^{2+} increases from 25 ppm to 50 ppm the IE slightly increases. This may be due to the fact that, when the concentration of Zn^{2+} increases, the Zn^{2+}-PAE complex formed in the bulk of the solution. After increasing concentration of PAE the IE decreases . This may be due to the fact that, when the concentration of PAE increases, the Zn^{2+}-PAE complex formed is precipitated in the bulk of solution [10-13].

3.2.Influence of immersion period on the inhibition efficiency of Pisonia Alba Extract (PAE):

The influence of duration of immersion on the IE of PAE (3 mL) - Zn^{2+} (50ppm) system is given in Table 3.When the immersion period increases the inhibition efficiency decreases and the corrosion rate increases this shows that theprotective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved,this same result is shown in Phyllanthusamarus extract [14].

Table 3: Influence of duration of immersion on the inhibition efficiency of PAE-Zn^{2+} system.

Immersion Period (days)	Corrosion Rate (CR) in the absence of the inhibitor (mmpy)	Corrosion Rate (CR) in the presence of the inhibitor PAE (3ml)+ Zn^{2+} (50 ppm) (mmpy)	Inhibition Efficiency (IE%)
1	0.8661	0.0685	92
3	0.9234	0.1565	83
5	0.9862	0.3245	67
7	1.3258	0.7556	43

3.3. Analysis of polarization curves

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 1. The corrosion parameters are given in Table 4. When carbon steel is immersed inwell water, the corrosion potential is -580 mV Vs SCE. The formulation consisting of 3 mL of PAE+ 50 ppm Zn^{2+} shifts the corrosion potential to -603mV Vs SCE. It shows that the corrosion potential is shifted to less negative side. The formulation consisting of PAE and Zn^{2+} shifts the anodic slopes and cathodic slopes (201.90 mV/dec and 198.52 mV/dec) almost equally controls both anodic and cathodic reaction . This suggests that the PAE-Zn^{2+} formulation performs as a mixed type inhibitor.The corrosion current value and LPR value for well water5.5431 × 10^{-5} A/$cm^2$and 963Ω cm^2. In the presence of the inhibitors, the corrosion current value has decreased to 1.0250 × 10^{-5} A/cm^2 and the LPR value has increased to 3130 Ω 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 well water containing 3mL of PAE and 50 ppm Zn^{2+} of by PAE–Zn^{2+} system [15].

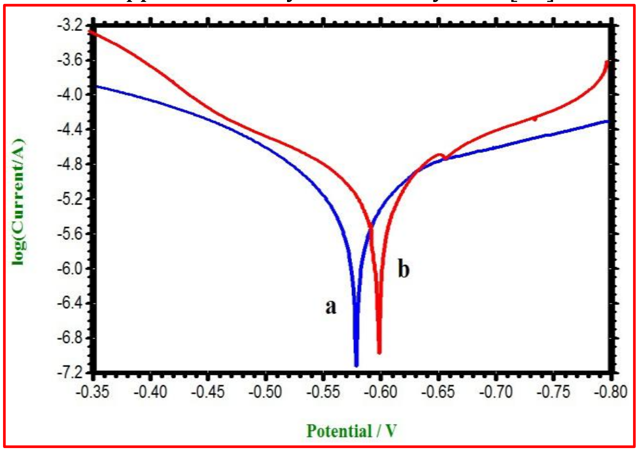


Fig. 1. Polarization curves of carbon steel immersed inwell water

a) well water

b) 3mL PAE + 50 ppm of Zn^{2+} + well water

Table 4: Corrosion parameters of carbon steel immersed in wellwater in the presence and absence of inhibitor obtained by polarization method:

Concentration		Tafel Parameters					IE (%)
PAE (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	
3	50	-603	1.0250 × 10^{-5}	201.90	198.52	3130	82

3.4. 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.2 AC impedance spectra have been used to detect the formation of film on the metal surface [16-21]. The impedance parameters, namely charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in Table 5.

When carbon steel is immersed in well water, R_{ct}value is 391Ω $cm^2$and C_{dl}value is 1.3137 × 10^{-6}μF/cm^2. When PAE and $Zn^{2+}$are added to well water, R_{ct}value increases from391Ω cm^2 to 2530Ω cm^2 and the C_{dl}value decreases from 1.3137 × 10^{-6}μF/$cm^2$to 0.0320 × 10^{-6}μF/cm^2. These results lead to the conclusion that a protective film is formed on the metal surface.The results obtained from Weight loss, Potentiodynamicpolarization study and AC impedance study indicate that inhibition efficiency are not same. Because of similar immersion times are not used when obtaining inhibition efficiency from various methods [22].

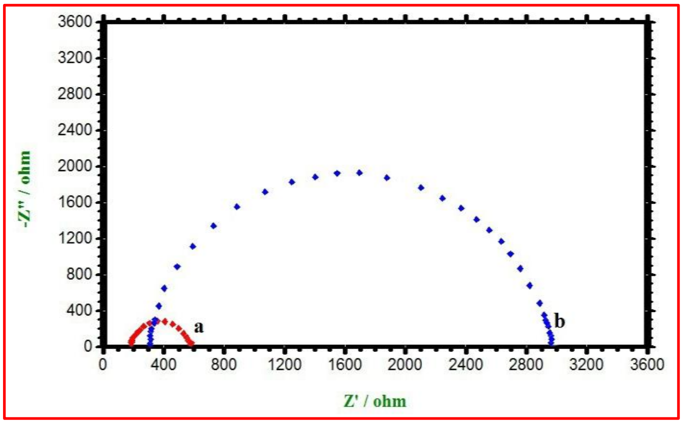


Fig. 2. AC impedance of carbon steel immersed in well water

a) well water
b) 3mL PAE + 50 ppm of Zn^{2+} + well water

Table 5: Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by AC impedance spectra:

PAE (mL)	Zn^{2+} (ppm)	R_{ct} (Ω cm^2)	C_{dl} ($\mu F/cm^2$)	IE (%)
0	0	391	1.3137×10^{-6}	85
3	50	2530	0.0320×10^{-6}	

3.5. Scanning electron microscopy (SEM)

SEM analysis was carried out to know additional information about the film Surface morphology of formation [23-24]. Figure 3.a shows polished carbon steel and Figure 3.b and 3.c show SEM photographs of carbon steel specimen in the absence and presence of the inhibitor system (3 mL of PAE and 50 ppm of Zn^{2+}). It can be seen from Figure 3.b shows that the surface is severely corroded and there is formation of different forms of corrosion products (iron oxides) on the surface in the absence of inhibitor. It further shows that the corrosion products appear very uneven and the surface layer is too rough. Figure 3.c shows that the surface of carbon steel immersed in the inhibitor solutions are having smooth surfaces. It is important to stress that when the inhibitor is present in the solution, the morphology of the carbon steel surface are quite different from the previous one. The protective layer is randomly observed on the mild surface and the interpretation is that due to adsorption of inhibitor on the carbon steel surface integrating into the passive film in an ordered manner has blocked the active site available in the metal surface of the carbon steel and thus corrosion process is inhibited.

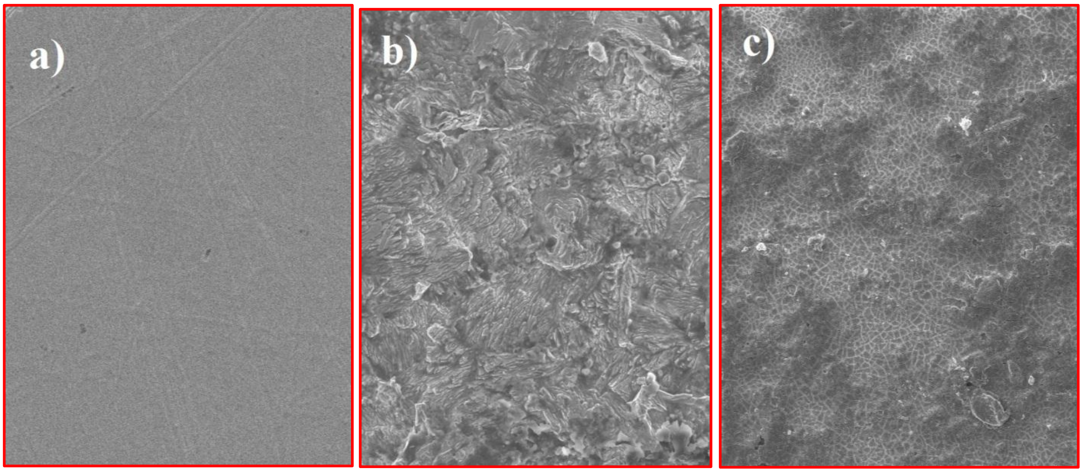


Fig.3. SEM images of
a) polished Carbon steel
b) carbon steel immersed in well water
c) carbon steel immersed in 3mL of PAE+ 50 ppm of Zn^{2+} + well water

4. CONCLUSIONS

From the overall experimental results the following conclusions can be deduced:

- The formulation consisting of 3mL of Pisonia Alba Extract (PAE) and 50 ppm of Zn^{2+} offers 92% inhibition efficiency to carbon steel immersed inwell water.
- When immersion period increases corrosion rate also increases.
- Potentiodynamic polarization study reveals that Pisonia Alba Extract (PAE) is good inhibitor and act as mixed type inhibitor for carbon steel corrosion in well water.
- AC impedance spectra reveals that double layer capacitances decrease with respect to blank solution when the plant extract is added. This fact confirms the adsorption of plant extract molecules on the carbon steel surface.
- SEM studies confirms that protective film formed on the carbon steel surface and thus corrosion process inhibited.

REFERENCE:

1. B. E. Amitha Rani; B. B. J. Basu, International Journal of Corrosion, 2012, 2012(1), 1-15.
2. AbdellahLaqhaili; AbdelhakHakiki; MahjoubaMossaddak; Maria Boudalia; AbdelkabirBellaouchou; Abdellah
3. Dr. S.K. Selvaraj, S. Priyanka, J. Jeyaseeli, International Journal for Research in Applied Science & Engineering Technology ,Volume 6 Issue IV, April 2018.
4. P.Angel , A. Sahaya Raja , J. Sathiyabama and V. Prathipa, International Journal of Chemical Studies , ISSN: 2321-4902, Vol. 2 ,Page-31, 2014.
5. K. Rajam,S. Rajendran, and R. Saranya, Journal of Chemistry, Volume 2013, Article ID 743807, 4 pagesJune 2012.
6. K. Anuradha, R. Vimala, B. Narayanasamy, J. A. Selvi, and S. Rajendran, Chemical Engineering Communications, vol. 195, no. 3, pp. 352–366, 2008.
7. M.Sangeetha, S.Rajendran, J.Sathiyabama and P.Prabhakar, J. Nat. Prod. Plant Resour., 2012, 2 (5):601-610
8. S. Rajendran, A. Raji, J. ArockiaSelvi, A. Rosaly and Thangasamy. Journals of Material Education 29: 245-258 (2007).
9. G.R.H. Florence, A.N. Antony J.W. Sahayaraj A.J. Amalraj, S. Rajendran, Indian J. Chem. Technol, 12 (2005) 472.
10. M . Elachouri, M . S. Hajji, M . Salem, S. Kertit, J. Aride, R.Coudert, E. Essassi,NACE, International, Corrosion, vol.52, no.2, p p .103-108, 1996.
11. M.G.Fortasa, Corrosion Engineering (New Delhi:Tata McGraw- Hill Publishing Company Ltd.,2006) 470.
12. K.P.Vinod Kumar, M.S.NarayananPillai, G.RexinThusnavis, Port ElectrochimActa (2010) 28 (6): 373-383.
13. A.Bouyanzer, B.Hammouti, L.Majidi et al. Port ElectrochimActa (2010) 28 (3): 165-172.
14. A.O.Odiongenyi, S.A.Odoemelam, N.O.Eddy, portugaliaeElectrochimicaActa (2009) 27 (1): 33-45.
15. P.K. Kasthuri, A. Arulanantham, Asian Journal of Chemistry (2010) 22(1): 430-434.
16. W.G.Y. Palmer, Corrosion, **7 (**1957)
17. Y.J. Qian, S. Turgoose, Br. Corros. J., 22 (1987) 268
18. M. Manivannan, S. Rajendran, International Journal of Engineering Science and Technology, ISSN : 0975-5462 Vol. 3 No.11 Nov-2011.
19. Ferreira, E.S., Giacomellic, C., Giacomellic,F.C., and Spinelli, A., Mater. Chem. Phys, (2004), 83 (1), 129-134.
20. Li, W.H., He, Q., Pei, C.L., and Hou, B.R., J. Appl. Electrochem, (2008), 38 (3), 289 – 295
21. T. Asokan, M. Sekar, C. Thangavelu, R. Sudhakaran and T. Kasilingam, Pelagia Research Library, Der ChemicaSinica, 2014, 5(6): 56-63
22. Apparao B.V., Christina K., Indian J. Chem. Technol. 13 (2006) 275.
23. Ghadah M. AL-Senani, Sameerah I. AL-Saeedi, Rasmiah S. AL-Mufarij, J. Mater. Environ. Sci. 7 (7) (2016) 2240-2251
24. R. Saratha, S.V. Priya and P. Thilagavathy, E-Journal of Chemistry,6(3),2009, pp. 785-795.