Research Journal of Chemical Sciences ____ ISSN 2231-606X
Vol. **3(2),** 10-15, February **(2013)** *Res. J. Chem. Sci.*

Inhibition of Corrosion of Carbon Steel in Sea Water by an Aqueous Extract of Eclipta alba Leaves – Zn^{2+} system

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Available online at: www.isca.in
Received 22nd September 2012, revised 2nd October 2012, accepted 2nd November 2012

Abstract

The Inhibition efficiency [IE] of an aqueous extract of eclipta alba leaves in controlling corrosion of carbon steel in sea water [Thondi, Tamil Nadu, India] has been evaluated by weight loss method. The weight loss study reveals that the formulation consisting of 6mL of EAE (Eclipta alba extract) and 25 ppm of Zn^{2+} has 92% inhibition efficiency in controlling corrosion of carbon steel in sea water. Polarization study reveals that EAE and Zn^{2+} system functions as mixed type inhibitor. The nature of the metal surface has been analysed by FTIR spectra and SEM analysis.

Keywords: Corrosion inhibition, Eclipta alba, carbon steel, sea water, SEM, FTIR.

Introduction

Seawater is one of the most corroded and most abundant naturally occurring electrolytes. The corrosivity of the seawater is reflected by the fact that most of the common structural metals and alloys are attacked by this liquid or its surrounding environments. The seawater environments can be divided into five zones namely: subsoil, continuously submerged, tidal, splash zone above high tidal and atmospheric zone[1].

Plant extracts are low-cost and biodegradable, and so the study of plant extracts as corrosion inhibitors is an important scientific research field due to both economic and environmental benefits. As early as in 1930, plant extracts (dried stems, leaves and seeds) of Chelidonium majus and other plants were used as corrosion inhibitors for steel in H_2SO_4 pickling baths[2]. In 1972, El Hosary et al.[3] studied the extract of Hibiscus subdariffa (Karkode) as the corrosion inhibitor for Al and Zn in HCl and NaOH solutions. In 1980s, Saleh et al.[4,5] reported the inhibition effect of aqueous extracts of some plant leaves (Opuntia, Aleo eru) and fruit peels (orange, mango) on the corrosion of steel, aluminum, zinc and copper in acids and aluminum in NaOH solution. In1990s, Azadirachta[6] and Vernonia amygdalina (bitter leaf)[7] leaves extracts were reported as good corrosion inhibitors for steel in HCl and H_2SO_4 solutions.

In the present research work the extract of Eclipta alba leaves is taken as it is a good corrosion inhibitor for carbon steel in marine media collected from Bay of Bengal at Thondi,a small town located in Ramnad District, Tamil Nadu, India. Eclipta alba, a medicinal herb is grown in many parts of India. The parts of the whole plant are used to cure many diseases. In ayirvedic medicine, the leaf extract is considered a powerful liver tonic, rejuvenative, and especially good eclipta prostrate is used for dyeing hair and tattooing[8-9].

Scheme-1
Leaves of Eclipta alba

The present work is undertaken: i. To evaluate the inhibition efficiency (IE) of Eclipta alba extract (EAE)-Zn^{2+} system in controlling corrosion of carbon steel immersed in sea water in the absence and presence of Zn^{2+} by weight loss method. ii. To study the mechanism of corrosion inhibition by polarization study iii. To analyse the protective film by FTIR spectra, scanning electron microscope (SEM), iv. To propose the mechanism of corrosion inhibition based on the above results.

Material and Methods

Preparation of plant extract: The leaves of Eclipta alba were dried and ground to powder and 10gm of the powdered leaves weighed and boiled with double distilled water, filtering the suspending impurities, and making up to 100mL. The extract was used as corrosion inhibitor in the present study.

Preparation of Specimen: Carbon steel specimens (0.02 6% S, 0.06% P, 0.4**%** Mn, 0.1% C and rest iron) of the dimensions 1.0 x 4.0 x 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

Weight – Loss Method: Carbon steel specimens were immersed in 100 ml of the medium containing various concentrations of the inhibitor 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 products were cleaned with Clarke's solution[10]. The corrosion 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, W_2 is the weight loss value in the presence of inhibitor, Corrosion rate was calculated using the formula[11], Corrosion rate (mm/year) = 87.6 W/ DAT.

Where W = weight loss in milligram, D = density of specimen g/cm^3, A = area of specimen in square cm,T=exposure time in hours.

Potentiodynamic Polarization Study: Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR 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 (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c were calculated and linear polarization study (LPR) was done. The scan rate (V/S0.01. Hold time at (E_{fcs}) was zero and quiet time (s) was two.

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 analyzed for surface analysis technique by FTIR spectra and scanning electron microscopy.

Fourier transform infrared spectra: These spectra were recorded in Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective flim was recorded by carefully removing the flim, mixing it with KBr and making the pellet.

Results and Discussion

The physicochemical parameters of sea water are given in table 1.

Table-1
Water analysis (Thondi sea water, Tamil Nadu, India)

Parameters	Result
Total dissolved salts (mg/L)	41881 ppm
Electrical conductivity (micro mhos/cm)	61589
pH	7.86
Total Hardness ($CaCO_3$ equivalent)	6100 ppm
Calcium as Ca (mg/L)	800 ppm
Magnesium as Mg (mg/L)	984 ppm
Sodium as Na (mg/L)	9800 ppm
Chloride as Cl (mg/L)	18256 ppm
Potassium as K (mg/L)	1300 ppm
Sulphate as SO_4 (mg/L)	1493 ppm

The calculated inhibition efficiencies (IE) of Eclipta alba Extract (EAE) in controlling the corrosion of carbon steel immersed in sea water both in the absence and presence of zinc ion have been tabulated in table 2. The calculated values indicate the ability of Eclipta alba Extract to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of zinc ion. The formulation consisting of 6mL of EAE and 25 ppm of Zn^{2+} offers 92% inhibition efficiency. That is mixture of inhibitors shows better IE than the individual inhibitors[12].

Potentiodynamic Polarization Study: Polarization study has been used to detect the formation of protective film on the metal surface. 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 figure-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 3.

When carbon steel is immersed in sea water the corrosion potential is -816 mV vs SCE. The formulation consisting of 6mL of EAE solution and 25 ppm of Zn^{2+} shifts the corrosion potential to -820 mV vs SCE. The corrosion potential shift is very small. This suggests that the EAE-Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction and cathodic reaction, to the same extent.

The corrosion current value and LPR value for sea water are 6.354×10^{-6} A/cm^2 and 6.500×10^3 ohm cm^2. For the formulation of EAE (6mL) and Zn^{2+} (25ppm), the corrosion current value has decreased to 5.863×10^{-6} A/cm^2 and the LPR value has increased to 6.909×10^3 ohm cm^2. This indicates that a protective 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[13-17].

Table-2
Corrosion inhibition efficiencies and the corresponding corrosion rates (millimeter per year) of EAE – Zn^{2+} system

Inhibitor HE (mL)	Zn^{2+}(ppm)					
	0		25		50	
	IE%	CR(mm/y)	IE%	CR(mm/y)	IE%	CR(mm/y)
0	-	0.1576	16	0.1323	47	0.0835
2	50	0.0788	65	0.0555	70	0.0472
4	55	0.0354	71	0.0457	76	0.0378
6	60	0.0630	92	0.0126	80	0.0315
8	63	0.0583	88	0.0189	82	0.0283
10	65	0.0555	80	0.0315	85	0.0236

Table-3
Potentiodynamic polarization curves of carbon steel immersed in various test solution

System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	I_{corr} A/cm^2
Sea water	-816	157	239	6.500 x 10^3	6.354 x 10^{-6}
Sea water + (6mL) EAE+ (25ppm) Zn^{2+}	-820	151	240	6.909 x 10^3	5.863 x 10^{-6}

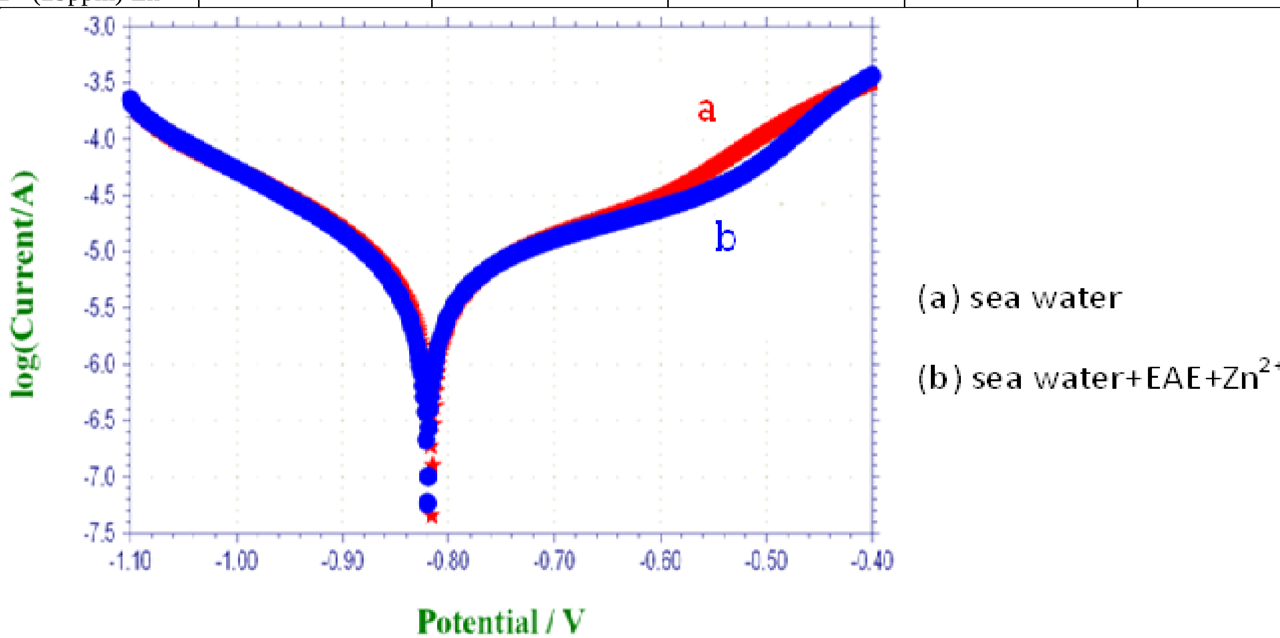
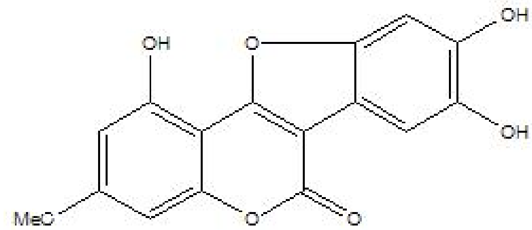


Figure-1
Polarization curves of carbon steel immersed in various test solutions

Analysis of FTIR spectra: The active principle in an aqueous extract of eclipta alba extract is wedelolactone. The green colour of the extract is due to wedelolactone.The main constituent of eclipta alba is wedelolactone. The structure of wedelolactone is shown in scheme 2. It contains 1,8,9-trihydroxy-3-methoxy- 6H-[1] benzofuro [3,2-c] chromen-6-one[18,19]. The wedelolactone extract was evaporated to dryness to set a solid mass. Its FTIR spectrum is shown in figure- 2a. The –OH stretching frequency appears at 3413cm^{-1}. The C=O stretching frequency appears at 1634cm^{-1}. The FTIR spectrum of the protective film formed on the surface of the metal after immersed in the solution containing 25 ppm of Zn^{2+} and 6 mL of EAE shown in figure-.2b. It is found that the -OH has shifted from 3413cm^{-1} to 3375cm^{-1}. The C=O stretching frequency has decreased from 1634cm^{-1} to 1596cm^{-1}. The ring oxygen appeared at 1090cm^{-1}. It has coordinated Fe^{2+} to form protective film on metal surface. The peak at 1365cm^{-1} is due to Zn-O stretching. So, it is concluded that $Zn(OH)_2$ is formed on cathodic sites of the metal surface[20].



wedelolactone

Scheme-2

structure of wedelolactone (extract of eclipta alba) 1,8,9-trihydroxy-3-methoxy- 6H-[1] benzofuro [3,2-c] chromen-6- one

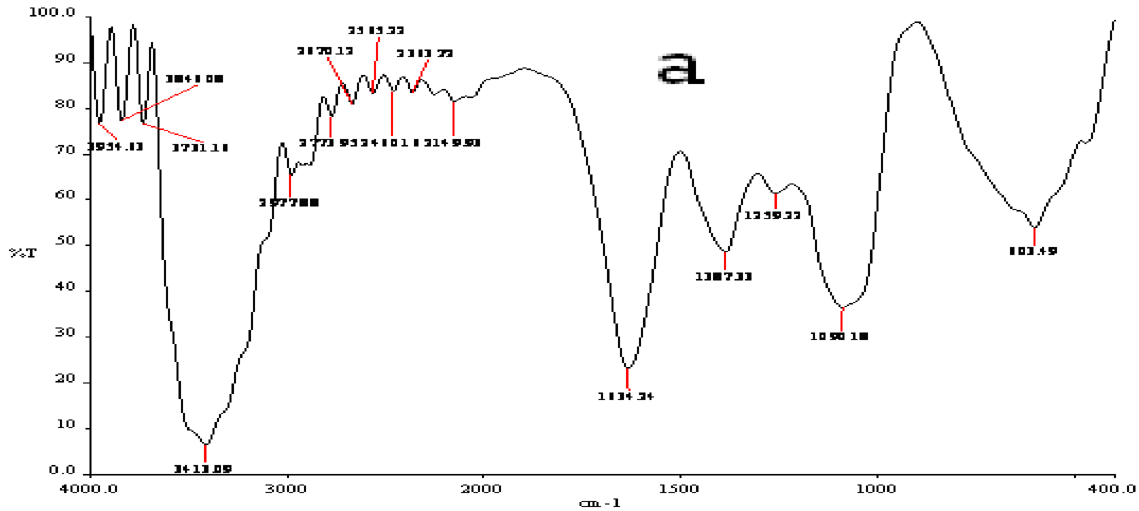


Figure-2a
FTIR spectrum of pure eclipta alba extract

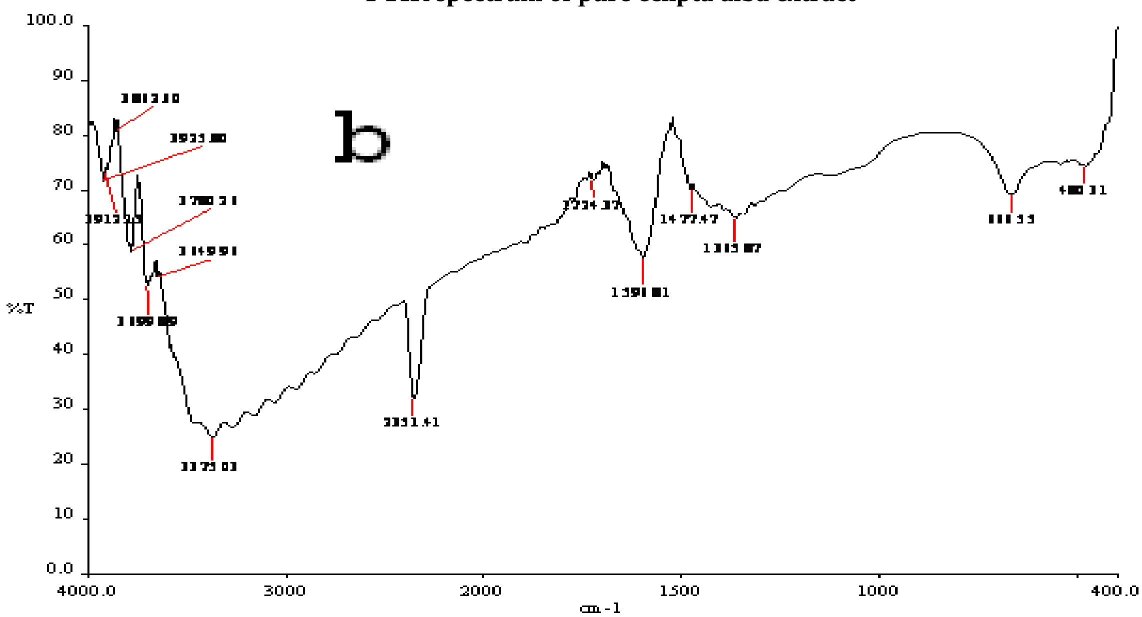


Figure-2b
FTIR spectrum of film formed on metal surface after immersion in sea water containing 6mL of EAE– 25 ppm Zn^{2+}

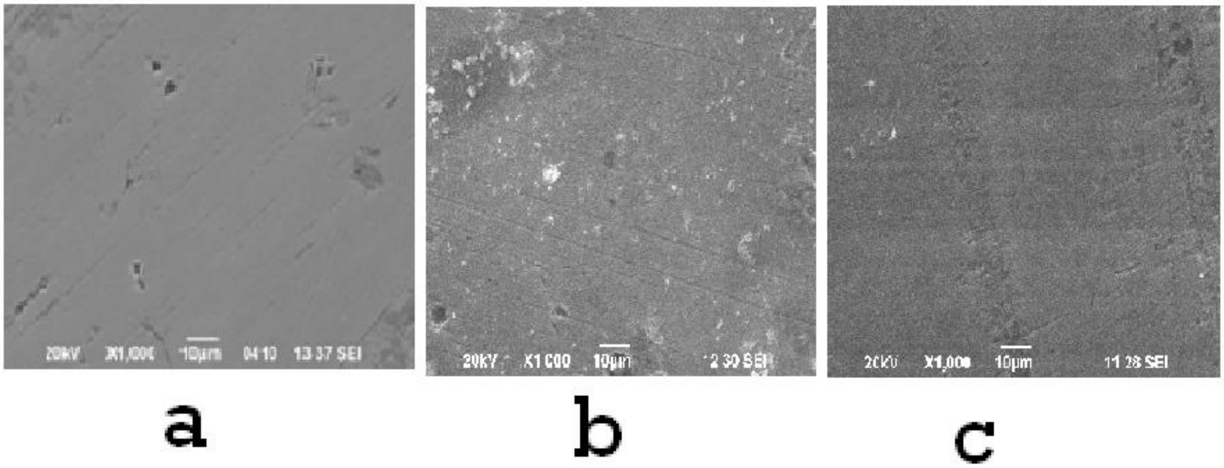


Figure-3
SEM micrographs of (a) polished Carbon steel (control) - Magnification-X1000, (b) Carbon steel immersed in sea water - Magnification-X1000, (c) Carbon steel immersed in sea water containing 6ml of EAE and 25 ppm of Zn^{2+} -Magnification-X1000

Scanning Electron Microscopy(SEM): The SEM images of magnification (X1000) of carbon steel specimen immersed in sea water for 1 day in the absence and presence of inhibitor system are shown in figure-3 image (b) and (c) respectively.The SEM micrographs of polished carbon steel surface (control) in figure-3 image (a) shows the smooth surface of the metal. This shows the absence of any corrosion products formed on the metal surface. The SEM micrographs of carbon steel surface immersed in sea water in figure-3 image (b) shows the roughness of the metal surface which indicates the corrosion of carbon steel in sea water. Figure-3 image (c) indicates that in presence of 6mL of EAE - Zn^{2+} (25ppm) mixture in sea water, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal EAE -Zn^{2+} inhibitor complex) and the surface is covered by a thin layer of inhibitors which control the dissolution of carbon steel. Such results have been earlier[21-24].

Mechanism of corrosion inhibition: Weight loss method reveals that the formulation consisting of 6mL of EAE and 25 ppm of Zn^{2+} offers 92% IE to carbon steel immersed in sea water. Polarization study reveals that EAE – Zn^{2+} system functions as a mixed inhibitor. FTIR spectra reveal that the protective film consists of Fe^{2+} - wedelolactone complex and $Zn(OH)_2$.

In order to explain the above facts in a holistic way, the following mechanism of corrosion inhibition is proposed. i. When the formulation consisting of sea water, eclipta alba extract and Zn^{2+} is prepared, there is formation of Zn^{2+} - wedelolactone complex in solution. ii. When carbon steel is immersed in the solution, the Zn^{2+} - wedelolactone complex diffuses from the bulk of the solution towards the metal surface. iii. On the metal surface, Zn^{2+} - wedelolactone complex is converted into Fe^{2+} - wedelolactone complex. Zn^{2+} is released

Zn^{2+} - wedelolactone + $Fe^{2+} \rightarrow$ Fe^{2+} - wedelolactone + Zn^{2+},

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

$$Zn^{2+} + 2OH^- \text{---------->} Zn(OH)_2 \downarrow$$

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

Conclusion

The present study leads to the following conclusions: The formulation consisting of 6 mL EAE and 25 ppm Zn^{2+} has 92% inhibition efficiency to carbon steel immersed in sea water. Polarization study reveals that EAE – Zn^{2+} system functions as a mixed inhibitor. FTIR spectra reveal that the protective film consists of Fe^{2+} - wedelolactone complex and $Zn(OH)_2$.

Acknowledgement

The authors are thankful to their respective management and University Grants Commission, New Delhi.

References

1. LaQue F.L., Marine corrosion and prevention, John Wiley & sons, 116 **(1975)**

2. Raja P.B. and Sethuraman M.G., Natural products as corrosion inhibitor for metal in corrosive Media – a review, *Mater. Lett.*, **62**, 113 -116 **(2008)**

3. El Hosary A.A., Saleh R.M., Shams El Din A.M., Corrosion inhibition by naturally occurring Substances, I. Effect of Hibiscus subdariffa (karkade) extract on the dissolution of aluminum and Zinc, *Corros. Sci.,* **12,** 897-904 **(1972)**

4. Saleh R.M., Ismail A.A., El Hosary A.A., Corrosion inhibition by naturally occurring Substances, V11, The effect of aqueous extracts of some leaves and fruit peels on the Corrosion of steel, aluminium, zinc and copper in acids, *Br. Corros. J.*, **17,** 131- 135 **(1982)**

5. Saleh R.M., Ismail A.A., El Hosary A.A., Corrosion inhibition by naturally occurring Substances, V11, The effect of aqueous extracts of some seeds, leaves, fruits peels on the Corrosion of aluminium in sodium hydroxide, *Corrs. Sci.*, **23,** 1239 - 1241 **(1983)**

6. Ekpe U.J., Ebenso E.E., Ibok U.J., Inhibitory action of Azadirachta leaves extract on Corrosion of mild steel in tetraoxosulphate (VI) acid, *J. West African Assoc.*, **37,** 13-30 **(1994)**

7. C.A. Loto The effect of *Vernonia amygdalina* (bitter leaf) solution extract on the Corrosion inhibition of mild steel, *Nig. Cor. J.*, **19,** 20-28 **(1998)**

8. Eclipta prostrate paramount for hair loss and alopecia citation of Bible. Healthy Hair Highlights News, 22 July 2011, Retrieved **(2011)**

9. Roy R.K., Thakur M., Dixit V.K., (Epub 2008 May 14), Hair growth promoting activity of Eclipta Prostrate in male albino rats, *Arch Dermatol Res.* 2008 Aug; **300(7),** 357-64 **(2012)**

10. Wranglen G., Synergistic effect of 2-chloroethyl phosphonic acid and Zn^{2+} Introduction to Corrosion and protection of Metals (Chapman & Hall, London) 236 **(1985)**

11. Fontana Mars G., Corrosion Engineering, TATA McGraw-Hill publishing company Limited, New Delhi, Third edition, 171 **(2006)**

12. Umamathi T., Arockia Selvi J., Agnesia Kanimozhi S., Rajendran S. and John Amalraj A., *Indian J. Chem. Technol*, **15,** 560-565 **(2008)**

13. Felicia Rajammal Selvarani, Santhamadharasi S., Wilson Sahayaraj J., John Amalraj A. and Susai Rajendran, *Bull. Electrochemistry.*, **20,** 561-566 **(2004)**

14. Johnairani V., Rajendran S., Sathiyabama J., Muthumegala T.S., Krishnaveni A. and Hajara Beevi N., *Bulgarian Chemical Communications.*, **44,** 41–51 **(2012)**

15. Kavipriya K., Sathiyabama J., Rajendran S. and Krishnaveni A., Surface morphology of protective film formed on carbon steel in presence of 2 – carboxyethyl phosphonic acid and Zn^{2+} system, *International journal of Advances in Engineering, Science and Technology.*, **2 (2),** 341 – 351 **(2012)**

16. Sangeetha M., Rajendran S., Sathiyabama J., Krishnaveni A., Shanthy P., Manimaran N. and Shyamaladevi B., Corrosion Inhibition by an Aqueous Extract of Phyllanthus Amarus, *Portugaliae Electrochimica Acta.*, **29 (6),** 429 – 444 **(2011)**

17. Manivannan M. and Rajendran S., Corrosion Inhibition of carbon steel by Succinic acid – Zn^{2+} system, *Research Journal of Chemical Sciences.*, **1(8)**, 42-48 **(2011)**

18. Neuropharmacological studies on Wedelia calendulacea Less stem extract. Prakash T., Rao N. Rama and Swamy A.H.M. Viswanatha, Phytomedicine, *International Journal of Phytotherapy & Phytopharmacology,* November **01**, **(2008)**

19. Muruganantham S., Anbalagan G. and Ramamurthy N., FT-IR and SEM-EDS analysis of medicinal plants Eclipta Alba hassk and Eclipta Prostrata linn, *ROMANIAN J. BIOPHYS.*,**19(4),** 285-294 BUCHAREST, **(2009)**

20. Robert M Silverstein Francis X. Webster Spectrometric Identification of Organic Compounds, Vl Edition, Wiley Student Edition, 108 **(2007)**

21. Xu Yang, Fu Sheng Pan and Ding Fei Zhang, A study on corrosion inhibitor for magnesium alloy, *Mat. Sci. Forum*, **610-613,** 920-926 **(2009)**

22. Gogoi P.K. and Barhai B., Corrosion Inhibition of carbon steel in open recirculating cooling water system of Petroleum refinery by a multi-component blend containing zinc (11) diethyldithio carbamate, *Indian J. Chem. Technology*, **17,** 291-295 **(2010)**

23. Hamdy A., Farag A.B., EL – Bassoussi A.A., Salah B.A. and Ibrahim O.M., Electrochemical behavior of brass Alloy in different saline media: Effect of Benzotriazole, *World App. Sci. Journal,* **8,** 565-571 **(2010)**

24. Weihua Li, Lichao Hu, Shengtao Zhang and Baorong Hou, Effects of two fungicides on the corrosion Resistance of copper in 3.5% Nacl solution under various conditions, *Corrosion Sci.*, **53,** 735-745 **(2011)**