International Journal of
Research in Chemistry and Environment
Available online at: www.ijrce.org
ISSN 2248-9649

Research Paper

Inhibition of Corrosion of Carbon Steel in Aqueous Medium using Naval Leaf Extract

Divya G., Sathiya M. and *Anbarasi C. Mary
PG and Research Department of Chemistry, Jayaraj Annapackiam College for Women, Periyakulam-625601, INDIA

(Received 18th June 2015, Accepted 16th October 2015)

Abstract: *Corrosion is a natural process generally known as rust, an unwanted phenomenon, which spoils the lustre and beauty of objects and shortens their life. The use of organic inhibitors is one of the most practical methods for protection against corrosion of metals and their alloys. In aqueous solutions, the inhibitory action of organic inhibitors is due to their physical (electrostatic) adsorption onto the metal surface, depending on the charge of the metal surface, the electronic structure of organic inhibitor and the nature of the medium. The present study is carried out to discuss the inhibitive effect of an aqueous extract of naval leaves on the corrosion of carbon steel in dam water using weight loss method, electrochemical studies and surface analysis techniques like Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM). Results of weight loss method indicated inhibition efficiency (IE) increased with increasing inhibitor concentration to a particular extend and then it decreases. Polarization study reveals that the inhibitor system controls the cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. The above results have been supported by surface morphology study using Scanning electron microscopy carried out on the carbon steel samples in the absence and presence of inhibitor.*

Keywords: Carbon steel, Corrosion inhibition, Synergistic effect, FTIR, SEM.

© 2016 IJRCE. All rights reserved

Introduction

Corrosion is the gradual damage of materials (usually metals) by chemical reaction with their environment. It is a steady and continuous problem, often difficult to get rid of completely. Prevention would be more practical and achievable than complete elimination. The use of inhibitor is one of the best options of protecting metals and alloys against corrosion [1]. Many synthetic compounds show excellent anticorrosive activity, but they are very toxic to both human being and environment, are costly and non-biodegradable. To reduce these problems natural products are used as corrosion inhibitors because they are non toxic, cheap, and biodegradable.

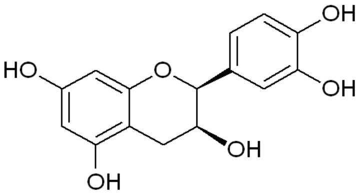
On going through that the literature, it was found that many plant extracts were used as corrosion inhibitors. Recently aqueous extract of banana peel [2], water Hyacinth (*Eichorrnia crassipes*) [3], *Hibiscus esculenta* leaves [4], garlic [5], Aloes extract [6], Asafetida [7], capsicum annum fruit extract [8], jeera (*Cuminum cyminum*) [9], propolis [10], Naval leaves [11] have been used as corrosion inhibitors. The present work focuses on the inhibitory action of various concentrations of naval leaf extract along with Trisodium citrate (TSC) in minimising the corrosion of carbon steel immersed in dam water. For the present study, the medium used is dam water collected from Sothuparai dam in the state of Tamil Nadu, India, constructed across the Vaigai River. A few industries located in downstream uses the dam water as coolant. The major constituent of naval leaf extract is Catechin.

Material and Methods

Sample Collection

Preparation of inhibitor (plant extract)

An aqueous extract of naval leaf was prepared by grinding 10 g of naval leaf, 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.



The molecular structure of Catechin

Preparation of the Specimen

The dimension and chemical composition of carbon steel samples are 1.0 cm × 4.0 cm × 0.2 cm. 0.026 % sulphur, 0.06 % phosphorous, 0.4 % manganese, 0.1 % carbon and the rest iron. They were polished with emery wheel and degreased with trichloroethylene and then stored in desiccators. Then they were used for the weight loss measurements and surface examination studies.

Weight-Loss Method

Carbon steel samples in triplicate were suspended in 100 ml of the Sothuparai dam water, containing various concentrations of the inhibitor, naval leaf extract (PE) in the absence and presence of Trisodium citrate (TSC) for a period of 3 days. The weights of the carbon steel before and after immersion were found out using a digital balance model AUY 220 SHIMADZU. The corrosion products were removed with acetone. The corrosion inhibition (IE) efficiency was then calculated using the equation

$$IE = 100\left[1 - \frac{W2}{W1}\right]\% \qquad (1)$$

Where, W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor.

Determination of corrosion rate

The Corrosion rate (CR) which is directly proportional to the weight loss / cm^3 in a specified time was calculated using the formula

$$\text{Mils penetration per year (mpy)} = \frac{534\ W}{DAT} \qquad (2)$$

Where,

W = weight loss in milligrams

D = density of specimen gm/cm^3 = 7.87 gm/cm^3

A = area of specimen in square inches = 1.55

T = exposure in hours = 72 hours

Potentiodynamic Polarization

Potentiodynamic polarization accountings were done using computer - controlled potentiostat, CHI electrochemical work station with impedance mode 608E. 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 βa and cathodic βc were determined and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at Ef(s) was zero and quiet time (s) was two.

AC Impedance Spectra

To record AC impedance spectra, the same instrument used for polarization study was used. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. From the above data charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Surface Examination Study

For surface examination studies, the carbon steel samples were immersed in the inhibited and uninhibited environment for a period of one day after which, they were taken out and dried. The film thus formed on the surface of the metal was subjected to various surface analysis techniques.

Fourier Transform Infrared Spectra (FTIR)

A Perkin-Elmer-1600 spectrophotometer was used to record FTIR spectra using KBr pellet method. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr, and making the pellet.

Scanning Electron Microscopy (SEM)

The carbon steel samples immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water and dried. SEM technique was used to examine the surface morphology. The morphology measurements of carbon steel were done using a JEOL model 6390 computer controlled scanning electron microscope.

Result and Discussion

Weight loss study

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

Table 1: Water Analysis

Parameter	Results
Appearance	Brownish
Total dissolved solids	90 ppm
Electrical conductivity	130
pH	Micromho/cm
Total hardness as $CaCO_3$	8.25
Calcium	45 ppm
Magnesium	10 ppm
Iron	06 ppm
Nitrate	10 ppm
Chloride	10 ppm
Sulphate	10 ppm
	02 ppm

The corrosion inhibition efficiency (IE) of PE in controlling the corrosion of carbon steel immersed in dam water, for a period of three days both in the absence and presence of TSC by weight loss method have been tabulated in table 2. The corresponding corrosion rates (CR) of carbon steel immersed in dam water are also given in table 2. It is observed that the IE increases upto a particular concentration of PE and then it decreases. When IE increases the corresponding corrosion rate decreases. The IE values indicate the ability of PE to act as a good corrosion inhibitor is enhanced significantly in the presence of TSC. A synergistic effect exists between PE and TSC. For example 6 ml of PE has 31% of IE and 25 ppm of TSC has 23 % of IE, and the formulation consisting of 6 ml of PE and 25 ppm of TSC has 94%. IE i.e., a mixture of inhibitors shows higher IE than the individual inhibitors [12-14]. This particular mixture of inhibitors is selected as the best system and using it further studies have been carried out. When the concentration of TSC is increased from 25 ppm to 50 ppm IE value decreases. Hence it is concluded that the optimum concentration of TSC for maximum IE is 25 ppm.

Table 2: Corrosion inhibition efficiencies (IE %) and the corresponding corrosion rates (CR) in (mills per year) of PE – TSC system

PE in ml	Tri Sodium Citrate					
	0 ppm		25 ppm		50 ppm	
	IE%	CR(mpy)	IE%	CR(mpy)	IE%	CR(mpy)
0	0	0.4742	23	0.3651	36	0.3034
2	16	0.3983	60	0.1897	48	0.2466
4	27	0.3461	61	0.1849	52	0.3225
6	31	0.3272	94	0.0239	46	0.2561
8	35	0.3082	59	0.1944	22	0.3699

Influence of immersion period

The influence of immersion period on the best system is shown in table 3. From table 3, it is found that the IE is low on the first day because the protective film is partially formed. On three days of immersion the IE is found to be high and the protective film is completely formed. After five days of immersion the IE is decreased because the protective film is broken due to the continuous attack of other ions present in the solution. On further increasing the immersion period again the protective film is formed and IE increases.

Table 3: Influence of Immersion period on the IE% of PE –TSC system

DAY	1	3	5	7
IE%	81	96	89	93

Analysis of polarization curves

Figure 1 refers to the potentiodynamic polarization curves of carbon steel in dam water in the absence and presence of inhibitor system. The cathodic branch represents the oxygen reduction reaction, while the anodic branch represents the iron dissolution reaction. The electrochemical parameter such as corrosion potential (E_{Corr}), corrosion current (I_{corr}), Tafel slopes (βa and βc) linear polarization resistance (LPR) are given in table 4. When carbon steel is immersed in dam water, the corrosion potential is -470 mV versus SCE. The best system shifts the corrosion potential to -810 mV versus SCE. i.e., the corrosion potential is shifted to the cathodic side. It is also noticed that the shift in the anodic slope (from 166 to 180 mV/dec) is lower than the shift in the cathodic slope (from 203 to 140 mV/ dec). Hence, it can be assumed that the same inhibitor system mostly controls the cathodic reaction. The corrosion current value and LPR value for dam water are 2.66×10^{-6} A/cm^2 and 2.05×10^4 ohm cm^2.

For the formulation of PE (4 ml) - TSC (25 ppm), the corrosion current value decreased to 4.92×10^{-7}A/cm^2 and the LPR value increased to 7.5×10^4ohm cm^2.

The information that the LPR value increases with decrease in corrosion current signifies the absorption of the inhibitor on the metal surface to block the active sites and slow down corrosion and bring down the corrosion rate [15, 16].

Table 4: Corrosion parameters of carbon steel immersed in dam water with and without the inhibitors obtained by polarization method.

PE in ml	TSC ppm	E_{Corr} mV VS SCE	I_{Corr} A/cm^2	βa mV/dec	βc mV/dec	LPR ohm cm^2
0	0	-470	2.66×10^{-6}	166	203	2.05×10^{4}
6	25	-810	4.92×10^{-7}	180	140	7.5×10^{4}

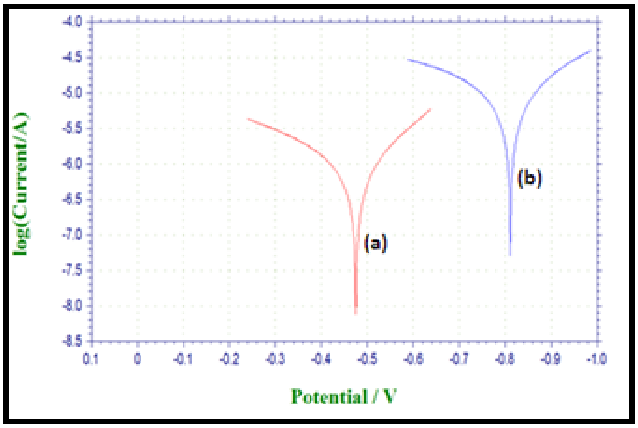


Figure 1: polarization curves of carbon steel immersed in solutions. a) dam water b) dam water containing 6 ml of PE and 25ppm of TSC

Analysis of AC impedance spectra

AC impedance spectra can be utilized to detect the formation of film on the metal surface [17, 18]. If a protective film is developed, the charge transfer resistance (R_t) increases and double – layer capacitance (C_{dl}) value decreases. Nyquist representations of carbon steel in dam water in the absence and presence of inhibitor system are shown in figure 2. The impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table 5. When carbon steel is immersed in dam water, R_t value is 1.08×10^{4} ohm cm^2 and C_{dl} is 8.36×10^{-10} F/cm^2.When 6 ml of PE and 25 ppm of TSC are added R_t value increases from 1.08×10^{4}ohm cm^2 to 4.01×10^{4}ohm cm^{2}and the C_{dl} value decreases from 8.36×10^{-10} F/cm^2 to 2.13×10^{-10} F/cm^2. This implies that a protective film is developed on the surface of the metal [19, 20].

Analysis of FT-IR spectra

FTIR spectra are used to analyze the protective film formed on the metal surface [21]. A few drops of an extract of naval leaf were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown in figure 3(a). The C=O stretching frequency appears at 1720 cm^{-1}. The OH stretching frequency is located at 3447 cm^{-1}. The C=C stretching frequency is seen at 1566 cm^{-1}. The symmetric C-O-C stretching frequency appears at 1396 cm^{-1}. Thus the structure of naval leaf extract (Catechin) is confirmed by FTIR spectrum. The FTIR spectrum (KBr) of pure TSC is given in figure 3(b).The peaks at1730 cm^{-1} and 1095 cm^{-1} are due to C=O C–O groups. The OH stretching frequency occurs at 3298 cm^{-1}. The bands at 2924 cm^{-1}, 2864 cm^{-1}, 951 cm^{-1} and 756 cm^{-1} are due to stretching and bending vibrations of methylene groups [22].

Table 5: Impedance parameters of carbon steel in dam water in the presence and absence of inhibitors obtained by AC impedance method

PE in ml	Nyquist plot	
	R_t ohm cm^2	C_{dl} F/cm^2
0	1.08×10^{4}	8.36×10^{-10}
6	4.01×10^{4}	2.13×10^{-10}

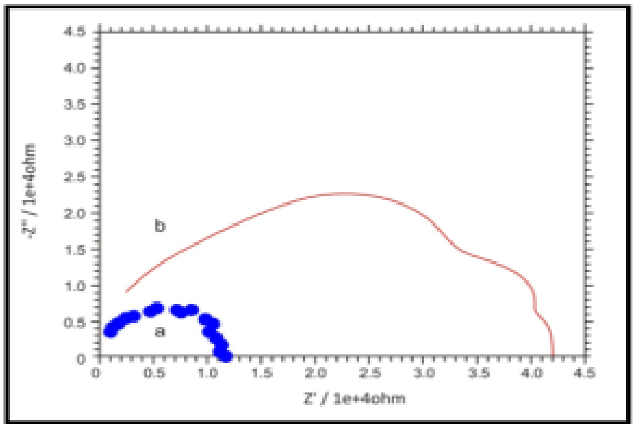


Figure 2: AC impedance spectra of carbon steel immersed in solutions: (a) dam water b) dam water containing 6ml of PE and 25 ppm of TSC

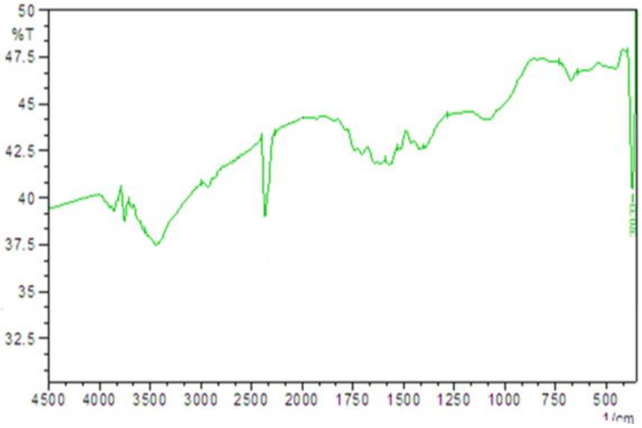


Figure 3(a): FT-IR spectrum of catechin extract evaporated to dryness

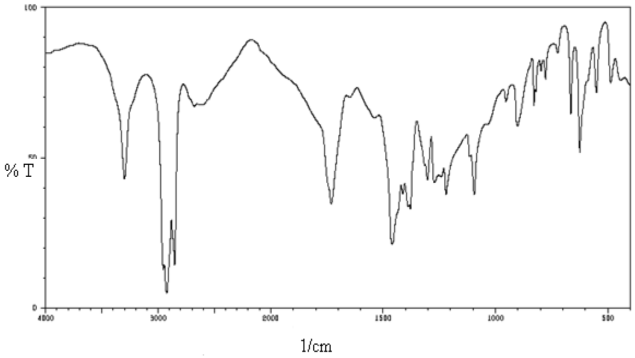


Figure 3(b): FT-IR spectrum of pure TSC

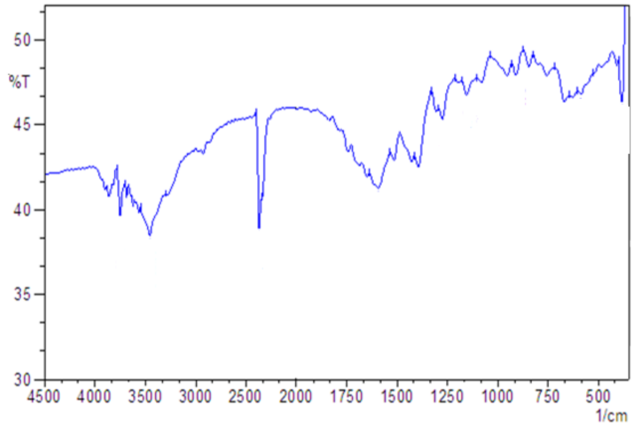
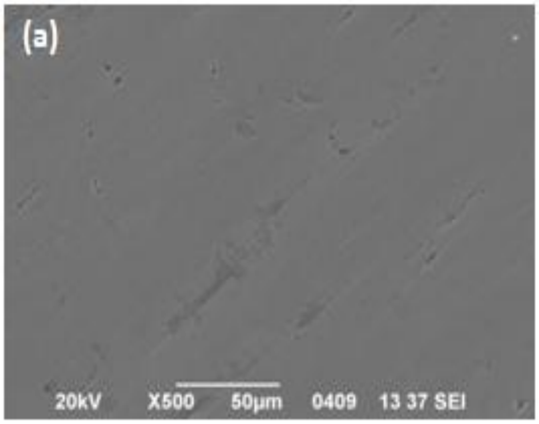


Figure 3(c): FT-IR spectrum of film formed on metal surface in presence of the inhibitors

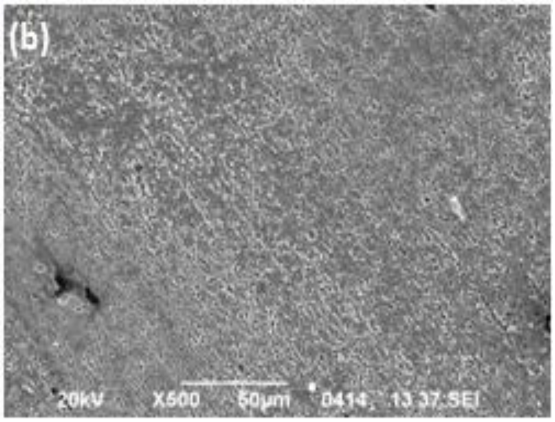
The FTIR spectrum of the film formed on the metal surface is shown in figure 3(c) the OH stretching frequency is shifted from 3447 cm^{-1} to 3453 cm^{-1}. The symmetric C-O-C stretching frequency is shifted from 1393 cm^{-1} to1396cm^{-1}. The C-O stretching frequency is decreased from 1095 cm^{-1}to 1078 cm^{-1}.These shifts signify that the electron clouds of OH, C-O-C and C-O are migrated towards Fe^{2+} resulting in the formation of Fe^{2+}– catechin and Fe^{2+}–TSC complexes on the anodic sites of the metal surface[23].

SEM Analysis of metal surfaces

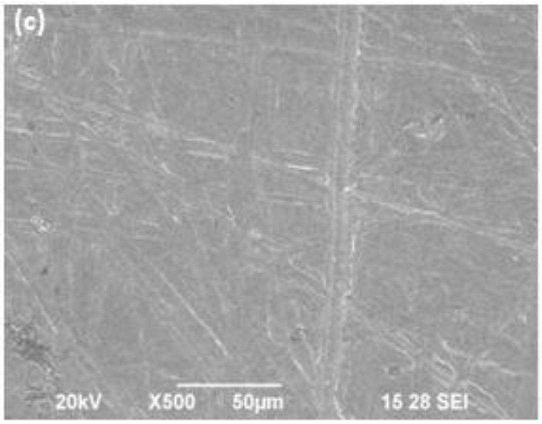
SEM provides a pictorial representation of the surface. SEM images of magnification 500 of carbon steel samples immersed in dam water for 1 day with and without the inhibitors are given in figure 4(b) and 4(c) respectively. The SEM micrograph of the polished carbon steel surface (control) is shown in figure 4(a). It confirms the smooth surface of the metal and lack of any corrosion products on the metal surface. The SEM micrograph of carbon steel surface immersed in dam water is given in figure 4(b). The metal surface is rough and uneven, which denotes the corrosion of carbon steel in dam water.



(a) Polished carbon steel (control) – magnification – X500



(b) Carbon steel immersed in dam water – magnification – X500



(c) Carbon steel in the inhibited environment. Magnification – X500

Figure 4: SEM micrographs

Figure 4(c) shows that in the presence of inhibitors in dam water, the surface coverage increases, which in turn indicates the formation of insoluble complex on the surface of the metal (Catechin and TSC inhibitor complex). A thin layer of the inhibitors covers the surface of the metal and controls the dissolution of carbon steel [24, 25].

Conclusion

The results of weights-loss study indicates that the formulation consisting of 6 ml of PE and 25ppm of TSC has 94% IE in reducing the corrosion of carbon steel in dam water. A synergistic effect exists between PE – TSC system. Polarization study indicates that the PE – TSC system predominantly controls the cathodic reaction. AC impedance and FT-IR spectra reveal that a protective film is formed on the metal surface. The SEM micrographs corroborate the formation of protective layers on the metal surface.

References

1.Amitha Rani B.E and Bharathi Bai, Basu J, Green Inhibitors for corrosion protection of Metals and Alloys, *Int. J.Corros*., 1(**2012**)

2.Sangeetha M., Rajendran S., Sathiyabama J., and Prabhakar P., Eco friendly extract of Banana peel as corrosion inhibitor for carbon steel in steel sea water, *Journal of natural product and plant resource*, **1(5)**, 14 (**2012**)

3.Kavitha N., Manjula P. Jeevanantham K, Synergistic effect of Water Hyacinth Leaves –Zn^{2+} system in corrosion inhibition of mild steel in aqueous medium, *Research Desk*, **3(1)**, 400 (**2014**)

4. Petchiammal A., Selvaraj S., and Kalirajan K,. Influence of Hibiscus esculenta leaves on the corrosion of stainless steel in acid medium, *Int. J. Universal Pharmacy and Bio Sciences*, **2(1)**, 2319 (**2013**)

5.Rajam K., Rajendran S., Saranya R., Allium Sativum (garlic) Extract as nontoxic corrosion inhibitor, *J. chem*, **2**, 1 (**2013**)

6.CangHui, FeiZhenghao, Shao Jinling, Shi Wenyan, Xu Qi, Corrosion Inhibition of mild steel by Aloes Extract in HCl solution medium, *Int. J. Electr chem. Sci*, **8**, 720 (**2013**)

7.Sangeetha M., Rajendran S., Sathiyabama J., and Prabhakar P., Asafoetida Extract (ASF) as green corrosion Inhibitor for Mild steel in Sea water, *Int. Research J. Environ. Sci.*, **1(5)**, 14 (**2012**)

8.Gopalji, Shukla S.K., Dwivedi P., Shanthi S., Eno E., E., Rajiv Prakash, Green Capsicum annuum Fruit Extract for Inhibition of Mild Steel Corrosion in Hydrochloric acid solution, *Int. J. Electrochem. Sci*, **7**, 12146 **(2012)**

9.Sribharathy V. and Susai Rajendran, cuminum cyanum extracts as Eco friendly corrosion inhibitor for mild steel in seawater, *ISRN Corros.*,**13**, 1 **(2013**)

10.Fouda1 A.S. and HamdyBadr A., Aqueous extract of propolis as corrosion inhibitor for carbon steel in aqueous solutions, *African J.Pure and Applied Chem.*, **7(10)**, 350 **(2013)**

11.Kavitha N., Manjula P., Anandhakumar N.**,** Syneristic effect of C. Naval Leaves Extract-Zn^{2+} in corrosion inhibition of mild steel in Aqueous medium, *Res. J. Chem. Sci.*, **4(8)**, 88 (**2014**)

12.Mary A.C., Rajendran S., Inhibition of corrosion of carbon steel by Heptane sulphonicacid –Zn^{2+} system, *J. Electrochem. Sci. Engg*., **2(1)**, 1 (**2012**)

13.Mary A.C., Rajendran S., Surface protection of carbon steel by Hexanesulphonic acid Zinc ion system, *ISRN Corros*, **1** (**2014**)

14.Mary Anbarasi et al., surface analysis of inhibitor film formed by butane sulphonic acid –Zn^{2+} system on carbon steel in aqueous medium, *Asian J. Chem.*, **24**, 5029 **(2012)**

15.Arockia S.J. et al., Analysis of nano film by atomic microscopy, *ZastitaMaterijala*, **50**, 91 (**2009**)

16.Kasthuri P.K., Arulanantham A., Ecofriendly extract of *Euphobia hirta* as corrosion inhibitor on mild steel in sulphuric acid medium. *Asian J. Chem.*, **22(1)**, 430 (**2010**)

17.Grosser F.N., Gonclaves R.S., Electro chemical evidence of caffeine adsorption on zinc surface in ethanol, *Corros. Sci.*, **50**, 2934 (**2008**)

18.Elayyachy M., El ldrissi A., Hammouti B., New thio compounds as corrosion inhibitor for steel in 1M HCl, *Corrros. Sci*., **48**, 470 (**2006**)

19.Shukla S.K., Quarishi M.A., 4-Substituted anilinomethylpropionate: New and efficient corrosion inhibitors for mild steel in hydrochloric acid solution, *Corrros. Sci*., **51**, 1990 (**2009**)

20.Vijayalakshmi P.R, Rajalakshmi R., Subhashini S., Corrosion Inhibition of Aqueous Extract of Cocos nucifera-Coconut Palm-Petiole Extract from Destructive Distillation for the Corrosion of Mild Steel in Acidic Medium, *Portu, Electrochim. Acta,* **29(1),** 9 (**2011**)

21.Lalitha, Ramesh S., Rajeswari S., Surface protection of copper in acid medium by azoles and surfactants, *Electrochim. Acta,* **51**, 47 (**2005**)

22.Robert M Silverstein and X. Francis, Webster Spectrometric Identification of Organic Compounds, VI Edition, Wiley Student Editon, 108 (**2007**)

23.Mary Anbarasi C., Susai Rajendran, Investigation of the inhibitive effect of octanesulphonic acid – zinc ion system on corrosion of carbon steel, *Chem. Engg.Commn,* 199, 1596 (**2012**)

24.Benita S., Nasser A.J.A., Rajendran S., Inhibitive action of hydro quinone – Zn^{2+} system in controlling the corrosion of carbon steel in well water, *Int. J. Engg. Sci. Technol.*, 341 (**2010)**

25.Amar et al, Synergistic corrosion inhibition study of armco iron in sodium chloride by piperidin -1-1-phosphonic acid- Zn^{2+} system, *Corros. Sci.*, **50**, 124 **(2008)**