INHIBITION OF CORROSION OF CARBON STEEL IN AQUEOUS MEDIUM USING PAPAYA LEAF EXTRACT

S. Anitha, G. Divya, M. Mala Jency, M. Sathiya and C. Mary Anbarasi
Post Graduate and Research Centre of Chemistry
Jayaraj Annapackiam College for Women (Autonomous),
Periyakulum, Theni Dist, Tamil Nadu, India
Email: anbuc_m@yahoo.co.in

Abstract

The inhibitive effect of papaya leaf extract on the corrosion of carbon steel in aqueous medium was investigated by using weight loss method, electrochemical studies and surface analysis techniques like Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM). The most suitable inhibitor concentration was found to be 4ml of papaya leaf extract and 25ppm of Tri sodium citrate has a 96% of inhibition efficiency. Polarization study reveals that the inhibitor system controls the anodic 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.

Key words: *Carbon steel; Corrosion inhibition; Synergistic effect; FTIR; SEM*

1. Introduction

Corrosion is the gradual destruction of materials (usually metals) by chemical reaction with their environment. It is a constant and continuous problem, often difficult to eliminate 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 good anticorrosive activity, and they are highly toxic to both human being and environment and they are expensive and non-biodegradable. To overcome these problems the natural products are used as corrosion inhibitors because they are non toxic, inexpensive, 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], have been used as corrosion inhibitors. The present work focuses on the inhibitory action of various concentrations of papaya leaf extract along with TSC in controlling the corrosion of carbon steel immersed in dam water. Papaya leaf contains major phyto chemicals such as carpaine, malic acid, quinic acid, a phenolic compound of manghaslin as an anti oxidant and also on enzyme papain [11].

2. Materials and methods

2.1. Preparation of plant extract

An aqueous extract of papaya leaf was prepared by grinding 10 g of papaya 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 major constituent of the aqueous extract is Manghaslin.

2.2. Preparation of the Specimen

Carbon steel specimens of dimension 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 with emery wheel and degreased with trichloroethylene and then stored in desiccator then it is used for the weight loss method and surface examination studies.

2.3. Weight-Loss Method

Carbon steel specimens were immersed in 100 ml of the Sothuparai dam water, containing various concentrations of the inhibitor (papaya) in the absence and presence of Trisodium citrate for a period of 3 days. 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. The corrosion inhibition efficiency was then calculated using the equation

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

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) is directly proportional to the weight loss / cm^3 in a specified time was calculated using the formula

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

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

2.4. Potentiodynamic Polarization

Potentiodynamic polarization measurements were performed 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 calculated 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.

2.5. AC Impedance Spectra

The same instrument used for polarization study was used to record AC impedance spectra also. 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.

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 analyzed by various surface analysis techniques.

Vol.3, No.1, December 2015 ISSN: 2347-9868

2.7. Fourier Transform Infrared Spectra (FTIR)

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.

2.8. Scanning Electron Microscopy (SEM)

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed Scanning Electron Microscopy to examine the surface morphology. The morphology measurements of carbon steel were examined using a JEOL model 6390 computer controlled scanning electron microscope.

3. Result and Discussion

3.1. Weight loss study

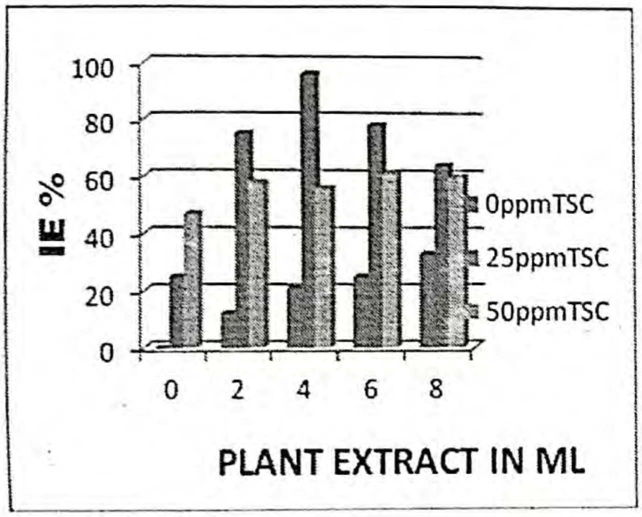
The physicochemical parameters of dam water are given in table 1.

The IE and the corresponding CR of papaya leaf extract (PE) – TSC systems are given in Table 2. It is found that the IE increases upto a particular concentration of papaya leaf extract. Then it decreases. When IE increases the corresponding corrosion rate decreases. A synergistic effect exists between papaya leaf extract and TSC. For example 4 ml of papaya leaf extract has 21% of IE and 25 ppm of TSC has 25 % of IE. However the formulation consisting of 4 ml of papaya leaf and 25 ppm of TSC has 96%. IE i.e., a mixture of inhibitors shows better IE than the individual inhibitors [12-14].

PARAMETER	RESULTS
Appearance	Brownish
Total dissolved solids	100 ppm
Electrical conductivity	140 Micromho/cm
pH	8.25
Total hardness as $CaCO_3$	50 ppm
Calcium	10 ppm
Magnesium	06 ppm
Iron	12 ppm
Nitrate	10 ppm
Chloride	10 ppm
Sulphate	02 ppm

Table 2: Corrosion inhibition efficiencies (IE%) and the corresponding corrosion rates (CR) in (mills per year) of papaya leaf extract – 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	25	0.3556	47	0.2513
2	12	0.4172	75	0.1185	58	0.1991
4	21	0.3746	96	0.0189	56	0.2086
6	25	0.3556	78	0.1043	61	0.1849
8	33	0.3177	64	0.1707	60	0.1896



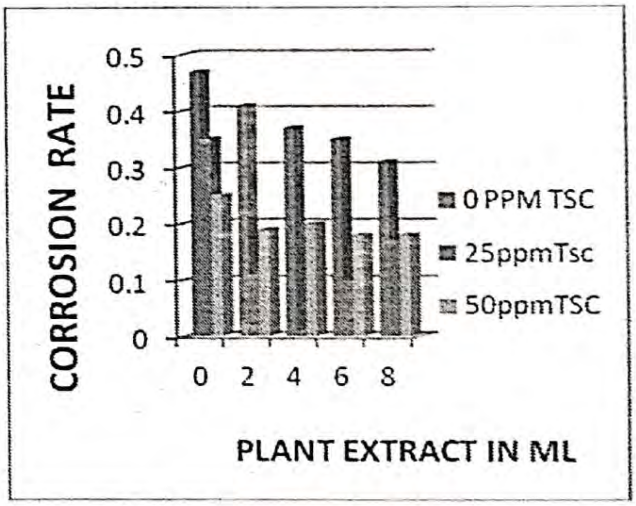


Fig. 1 Graph of Corrosion inhibition efficiencies (IE%) and the corresponding corrosion rates (CR) in (mills per year) of papaya leaf extract – TSC system.

3.2. Synergism parameter (S_I)

Synergism parameter (S_I) is an indication of synergistic effect between inhibitors [15,16]. When synergism parameter value is greater than one, synergistic effect exists between the inhibitor. Synergism parameter value is found to be greater than one indicating synergistic effect exists between 25 ppm of TSC with various concentration of papaya leaf extract. In the case of 50 ppm of TSC, synergistic effect exists with two concentrations of the plant extract (2 and

6) ml. In these two cases, the synergism parameter value is greater than one. But for the other two cases (4 and 8 ml) the synergism parameter value is less than one. So no synergistic effect exists between inhibitors. The results are given in table 3.

$$S_I = 1 - I_{1+2} / 1 - I'_{1+2}$$

Where

$$I_{1+2} = (I_1 + I_2) - (I_1 \times I_2)$$

I_1 = surface coverage of inhibitor (papaya leaf extract)

I_2 = surface coverage of inhibitor (TSC)

$(I_1 \times I_2)$ = combined surface coverage of inhibitors (papaya leaf extract – TSC)

Surface coverage = inhibition efficiency /100

I_2 for TSC (25 ppm) = 0.25, (50 ppm) =0.47

Table 3: Synergism parameter (S_I)

		I_2 =0.25		I_2=0.47	
PE	I_1	PE-TSC (25 ppm) I'(1+2)	S_1	PE-TSC (50 ppm) I'(1+2)	S_1
2	0.12	0.75	2.64	0.58	1.110
4	0.21	0.96	14.81	0.56	0.9575
6	0.25	0.78	2.55	0.61	1.0192
8	0.33	0.64	1.395	0.60	0.8877

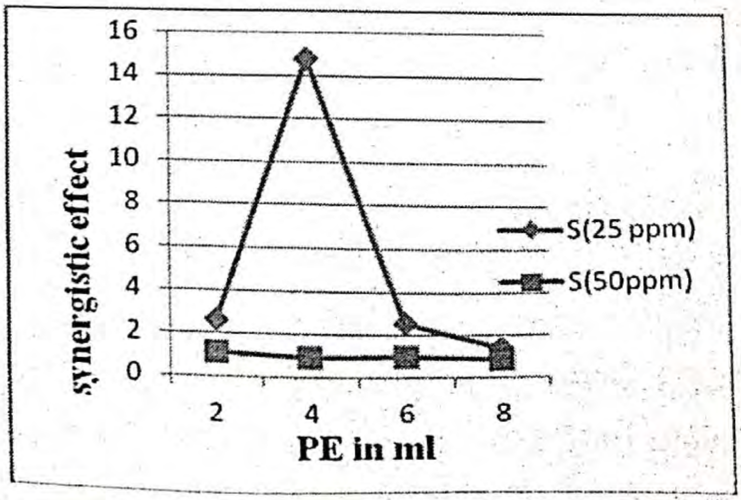


Figure 3: Graph of synergism parameters

3.3. Influence of immersion period

The influence of immersion period on IE of papaya leaf extract (4 ml) and TSC (25 ppm) is shown in figure-4. From Table 4, it is found that the IE is low on the first day because the protective film is partially formed. After three days the IE is found to be high and the protective film is completely formed. After five days again 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 4: Immersion period on the IE% of papaya leaf extract –TSC system immersed in dam water.

	Immersion period				
DAY	1	3	5	7	10
IE%	81	96	89	93	88

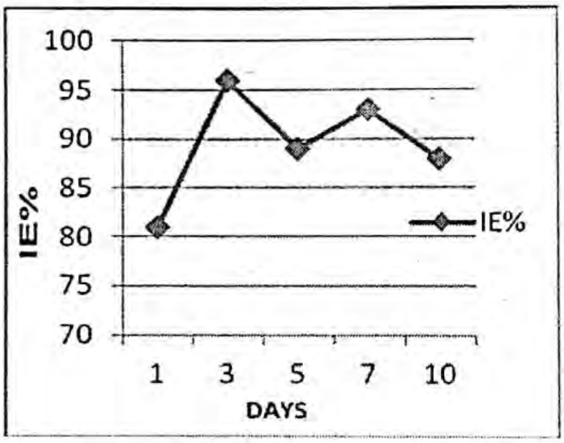


Figure 4: Influence of immersion period on the IE of papaya leaf extract–TSC system immersed in dam water.

3.4. Analysis of polarization curves

Figure 5 represents 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 (ßa and ßc) liner polarization resistance (LPR) are given in Table V. When carbon steel is immersed in dam water, the corrosion potential is -470 mV versus SCE. The formulation consisting of papaya leaf extract (4ml) and TSC (25 ppm) shifts the corrosion potential to -403 mV versus SCE. i.e., the corrosion potential is shifted to the anodic side. It is also observed that the shift in the anodic slope (from 166 to 200 mV/dec) is greater than the shift in the cathodic slope (from 203 to 210 mV/dec). Hence, it can be said that the same inhibitor system predominantly controls the anodic 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 papaya leaf extract (4 ml) - TSC (25 ppm), the corrosion current value decreased to 4.56×10^{-7}A/cm^2 and the LPR value increased to 8.3×10^4ohm cm^2. The fact that the LPR value increases with decrease in corrosion current indicates absorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate [17,18].

Table 5: Corrosion parameters of carbon steel immersed in dam water in the presence and absence of inhibitor obtained by polarization method

PE in ml	TSC ppm	E_{Corr} mV VS SCE	I_{Corr} A/cm^2	βa	βc	LPR ohm cm^2
0	0	-470	2.66×10^{-6}	166	203	2.05×10^4
4	25	-403	4.56×10^{-7}	200	210	8.3×10^4

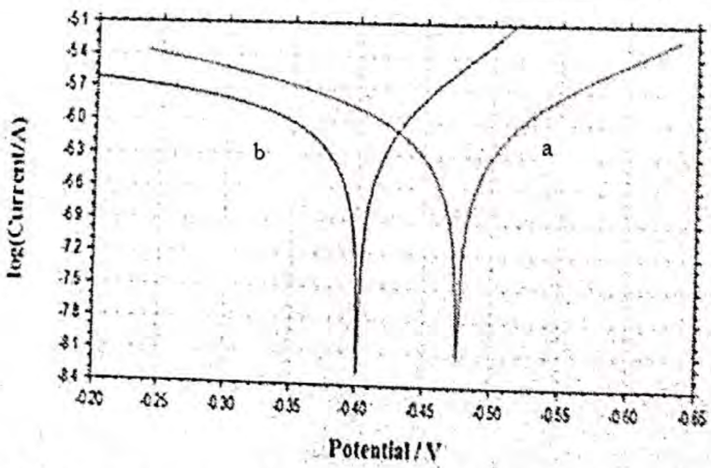


Figure 5: Polarization curves of carbon steel immersed in various test solutions. a) dam water b) dam water containing 4 ml of papaya leaf extract and 25ppm of TSC.

3.5. Analysis of AC impedance spectra

AC impedance spectra can be used to detect the formation of film on the metal surface. If a protective film is formed, the charge transfer resistance (R_t) increase 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 6. The impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table VI. When carbon steel is immersed in dam water, R_t value is 1.084×10^4 ohm cm^2 and C_{dl} is 8.359×10^{-10} F/cm^2.When 4 ml of papaya leaf extract and 25 ppm of TSC are added R_t value increases from 1.084×10^4ohm cm^2 to 3.6×10^4ohm cm^{2}and the C_{dl} value decreases from 8.359×10^{-10} F/cm^2 to 3.8×10^{-10} F/cm^2.This suggests that a protective film is formed on the surface of the metal [19,20].

Table 6: Impedance parameters of carbon steel in dam water in the presence and absence of inhibitors obtained by AC impedance method

System	Nyquist plot	
	R_t ohm cm^2	C_{dl} F/cm^2
Dam water	1.084×10^4	8.359×10^{-10}
TSC+PLE	3.6×10^4	3.8×10^{-10}

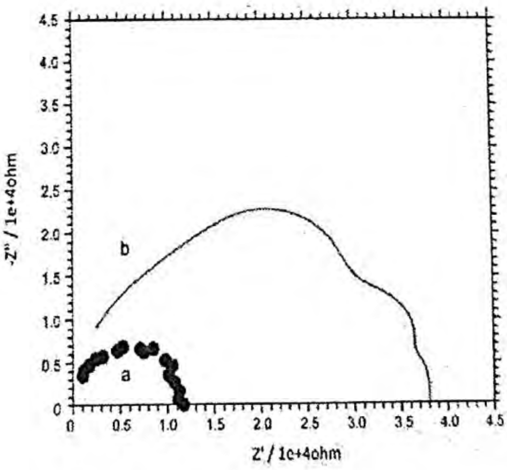
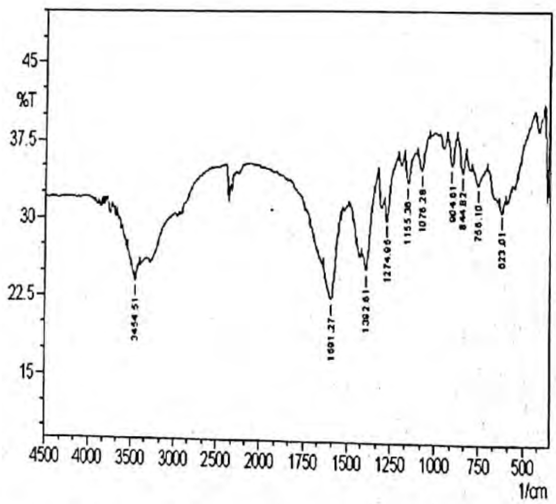


Figure 6: AC impedance spectra of carbon steel immersed in various test solution: (a) dam water b) dam water containing 4 ml of papaya leaf extract and 25ppm of TSC.

3.6. Analysis of FT-IR spectra

Earlier researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [21, 22]. FTIR spectra have been used to analyze the protective film formed on metal surface. Papaya leaf contains carpine, malic acid, quinic acid, and a phenolic compound manghasline.

A few drops of an extract of papaya leaf were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown in figure 7(a). The O-H stretching frequency appears at 3454 cm^{-1}. The C=C stretching frequency is seen at 1591 cm^{-1}. The C-C stretching frequency appears at 1392 cm^{-1}. The C-O stretching frequency is located at 1274 cm^{-1}. Thus the structure of papaya leaf extract is confirmed by FTIR spectrum. The FTIR spectrum (KBr) of pure TSC is given in figure 7(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}, 951cm^{-1} and 756 cm^{-1} are due to stretching and bending vibrations of methylene groups.



The FTIR spectrum of the film formed on the metal surface shown in fig 7(c). The C-O stretching frequency is shifted from 1274 cm^{-1} to 1309 cm^{-1}.The C=O stretching frequency has increased from 1730 cm^{-1} to 1743 cm^{-1}. These shifts indicate that the electron clouds of C-O and C=O bonds are shifted towards Fe^{2+} resulting in the formation of Fe^{2+} – manghasline and Fe^{2+}–TSC complexes on the anodic sites of the metal surface [23].

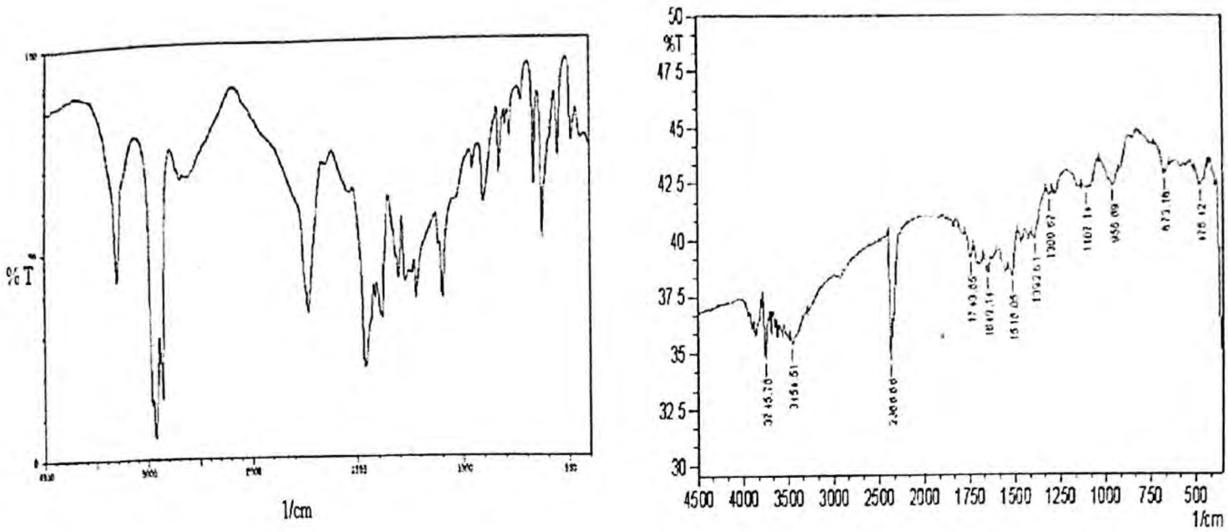


Figure 7(a): FT–IR spectrum of papaya leaf extract. (b) FT-IR spectrum of pure TSC Figure 7(c) FT-IR spectrum of film formed on metal surface after immersion in dam water containing 4 ml of papaya leaf extract and 25 ppm of TSC.

3.7. SEM Analysis of metal surfaces

SEM images of magnification 500 of carbon steel specimens immersed in dam water for 1 day in the absence and presence of inhibitors system are shown in figure 8(b) and 8(c) respectively. The SEM micrograph of the polished carbon steel surface (control) is shown in figure 8(a). It shows the smooth surface of the metal and absence of any corrosion products formed on the metal surface. The SEM micrograph of carbon steel surface immersed in dam water is given in figure 8(b). The metal surface is rough, which indicates the corrosion of carbon steel in dam water.

Figure 8(c) indicates that in the presence of 4 ml of papaya leaf extract and 25 ppm of TSC mixture in dam water, the surface coverage increases, which in turn results in the formation of insoluble complex on the surface of the metal (manghasline and TSC inhibitor complex). The surface is covered by a thin layer of inhibitors that control the dissolution of carbon steel [24, 25].

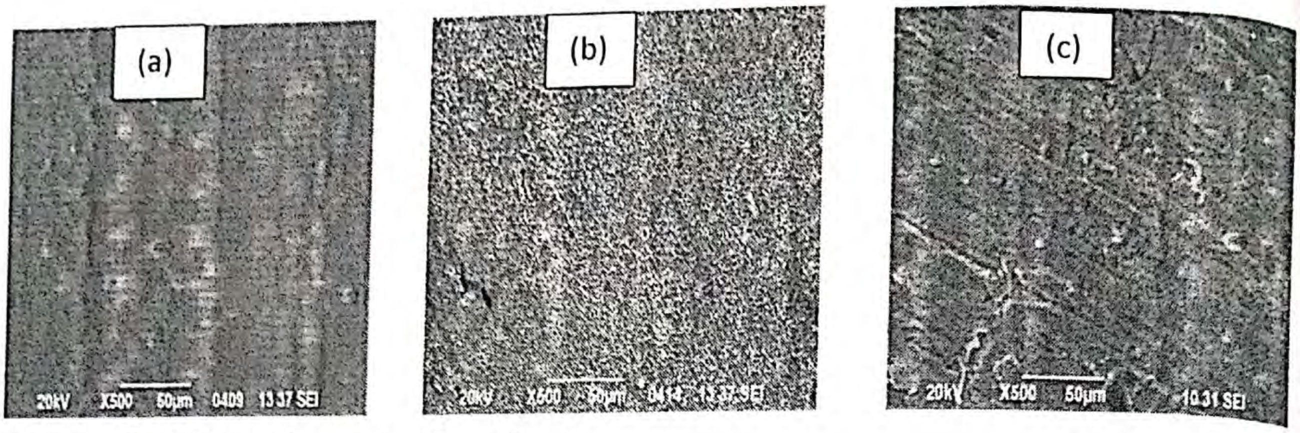


Figure 8: SEM micrographs of

a) **Polished carbon steel (control) – magnification – X500**
b) **Carbon steel immersed in dam water – magnification – X500**
c) **Carbon steel immersed in dam water containig 4 ml of papaya leaf extract and 25 ppm of TSC. Magnification – X500**

4. Conclusion

The results of weights-loss study show that the formulation consisting of 4 ml of papaya leaf extract and 25ppm of TSC has 96% IE in controlling the corrosion of carbon steel in dam water. A synergistic effect exists between papaya leaf extract – TSC system. Polarization study reveals that the papaya leaf extract – TSC system predominantly controls the anodic reaction. AC impedance and FT-IR spectra reveal that a protective film is formed on the metal surface. The SEM micrographs confirm the formation of protective layers on the metal surface.

5. Reference

[1] Amitha Rani B.E and Bharathi Bai, Basu J, Green Inhibitors for corrosion protection of Metals and Alloys, *International journal of corrosion*, vol. 2012, pp. 15 pages.

[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*, vol. 1(5),2012, pp. 14-21.

[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*, vol. 3(1), 2014, pp. 400-409.

[4] Petchiammal A., Selvaraj S., and Kalirajan K,. Influence of Hibiscus esculenta leaves on the corrosion of stainless steel in acid medium, *International Journal of Universal Pharmacy and Bio Sciences,* vol. 2(1), 2013, pp. 2319-8141.

[5] Rajam K., Rajendran S., Saranya R., Allium Sativum (garlic) Extract as nontoxic corrosion inhibitor, *Journal of chemistry,* vol. 2013, pp. 4 pages.

[6] CangHui, FeiZhenghao, Shao Jinling, Shi Wenyan, Xu Qi, Corrosion Inhibition of mild steel by Aloes Extract in HCl solution medium, *International Journal of Electro chemical science,* vol. 8, 2013, pp. 720-734.

[7] Sangeetha M., Rajendran S., Sathiyabama J., and Prabhakar P., Asafoetida Extract (ASF) as green corrosion Inhibitor for Mild steel in Sea water, *International Research Journal of Environment Sciences,* vol. 1(5), 2012, pp. 14-21.

[8] Gopalji, Sudhish Kumar Shukla, PriyankaDwivedi, ShanthiSundaram, Eno E., Ebens, Rajiv Prakash, Green Capsicum annuum Fruit Extract for Inhibition of Mild Steel Corrosion in Hydrochloric acid solution, *International Journal of electrochemical science,* vol.7, 2012, pp.12146-12158.

[9] Sribharathy V. and Susai Rajendran, cuminum cyanum extracts as Eco friendly corrosion inhibitor for mild steel in seawater, *ISRN corrosion,* vol. 2013, 2012, pp. 7 Pages.

[10] Fouda1 A.S. and HamdyBadr A., Aqueous extract of propolis as corrosion inhibitor for carbon steel in aqueous solutions, *African journal of pure and applied Chemistry,* vol.7 (10), 2013, pp. 350-359.

[11] Kavitha N., Manjula P., Anandhakumar N., Syneristic effect of C. Papaya Leaves Extract-Zn2+ in corrosion inhibition of mild steel in Aqueous medium, *Research Journal of Chemical Sciences* 4(8), 2014, pp. 88-93.

[12] Mary Anbarasi C., Susai Rajendran, Electrochem. Sci. Engg., vol. 2(1), (2012), 1-18.

[13] Mary Anbarasi C., Susai Rajendran, *ISRN Corrosion,* (2014) pp. 1-8.

[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 Journal of Chemistry,* Vol. 24, 2012, pp. 5029-5034.

[15] Arockia Selvi J.et al., Analysis of nano film by atomic microscopy, *Zastita Materijala,* vol. 50, 2009, pp. 91-98.

[16] Kasthuri P.K., Arulanantham A., Ecofriendly extract of Euphobia hirta as corrosion inhibitor on mild steel in sulphuric acid medium. *Asian Journal of Chemistry,* vol. 22(1), 2010, pp. 430-434.

[17] Grosser F.N., Gonclaves R.S., Electro chemical evidence of caffeine adsorption on zinc surface in ethanol, *Corrosion Science,* vol. 50, 2008, pp. 2934 -2938.

[18] Elayyachy M., El ldrissi A., Hammouti B., New thio compounds as corrosion inhibitor for steel in 1M HCl, *Corrrosion Science.,* vol. 48, 2006, pp. 470-2479.

[19] Shukla S.K., Quarishi M.A., 4-Substituted anilinomethylpropionate: New and efficient corrosion inhibitors for mild steel in hydrochloric acid solution, Corrosion Science, vol. 51, 2009, pp. 1990-1997.

[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, *Port Electrochim Acta vol.* 29(1) 2011, pp. 9-21.

[21] Lalitha, S. Ramesh, Rajeswari S., Surface protection of copper in acid medium by azoles and surfactants, *Electrochimica Acta,* vol. 51, 2005, pp. 47-55.

[22] Robert M Silverstein and X. Francis, Webster Spectrometric Identification of Organic Compounds, VI Edition, Wiley Student Editon, 2007, pp. 108.

[23] Mary Anbarasi C., SusaiRajendran, Investigation of the inhibitive effect of octanesulphonic acid - zinc ion system on corrosion of carbon steel, *Chemical Engineering and Communication,* vol. 199, 2012, pp. 1596-1609.

[24] Benita Sherine, Jamal Abdul Nasser A., Rajendran S., Inhibitive action of hydro quinone – Zn^{2+} system in controlling the corrosion of carbon steel in well water, *International journal of Engineering Science and Technology,* vol. 2 2010, pp. 341-357.

[25] Amar et al., Synergistic corrosion inhibition study of armco iron in sodium chloride by piperidin -1-1-phosphonic acid- Zn^{2+} system, Corrosion Science, vol. 50, 2008, pp. 124-130.