International Journal of Engineering & Technology, 7 (3.6) (2018) 322-329

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

A Green Approach to Preparing Bio-Inhibitor for Mild Steel Corrosion in Different Acid Mediums

N. Poongothai[1*], R. Athira[2], P.K. Neena[3]

[1]*Amrita Vishwa Vidyapeetham, Coimbatore, Tamil Nadu, India.*
[2]*Amrita Vishwa Vidyapeetham, Coimbatore, Tamil Nadu, India.*
[3]*Amrita Vishwa Vidyapeetham, Coimbatore, Tamil Nadu, India.*
**Corresponding Author E-Mail:Npgothai@Gmail.Com*

Abstract

Inhibition efficiency (I. E) of various concentrations of Carica Papaya (C. P)extracts on the corrosion of mild steel (MS) in 1M HCl and 0.5M H_2SO_4medium was investigated by weight loss and electrochemical methods at room temperature and elevated temperature. Acid extract of C. P was characterized by using FTIR and XRD spectral studies to identify the major constituents present in it. Zeta potential and EDAX analysis were carried out for the extract to identify electrochemical aspect of a particle's surface, and information about a particle's dispersibility, aggregability, and adhesion ability can be obtained from this measurement. Surface analysis studies such as FESEM and contact angle measurement were carried out for the C. P extracts to locate the surface coverage of the inhibitor and confirm the hydrophilic nature on the metal surface. Langmuir and Temkin adsorption isotherm confirm the mono layer adsorption and heterogeneity of the MS surface. Thermodynamic data's such as activation energy, Gibbs free energy, enthalpy and entropy changes were calculated using weight loss measurements data at room as well as elevated temperatures and identified free energy of adsorption and exothermic reaction taking place during corrosion process. Phytochemical studies confirm the presence of chemical constituents with hetero atom that provide more I.E due to its adsorption of inhibitor on metal surface.

Keywords: *Mild steel, inhibitor, adsorption, inhibition efficiency.*

1. Introduction

There is a vast increase in usage of metals in all fields of technology and use of rare, expensive metals whose protection requires special precautions. In every walk of our life, we use new high strength alloys which are usually susceptible to certain types of corrosive attacks. Corrosion is a costly and severe material science problem. As resources are consumed in due course of time, if not immediately conserved and recycled, will become watch wards, not catch wards. There are two types of scales are formed on the metal surface during exposure, viz high temperature scale (Wurztite, Magnetite& Hematite) and low temperature scale (Magnetite and Hematite) [1]. Before making protective coatings like painting, the rust on metal surface must be removed by acid pickling. During acid pickling, not only the scale deposited on metal surface gets removed but metal dissolution also takes place leading to thinning of metal and reduction of its strength. These forms of corrosion and metal dissolution can be prevented by proper choice of materials or by use of inhibitors or cathodic protection [2]. The important factors influencing corrosion inhibition are the nature of bonding and the effect of the structure of the adherent compound on the strength and stability of the bond, paving the way for the concept of the two-dimensional quasi compounds [3]. The surface film retards the anodic process or the cathodic process or both. The surface film also impedes the reactant or product transfer or influences the rate constant, the net effect is inhibition [4]. The extracts of some common plants and by-products contain different organic compounds (e.g) amino acids, alkaloids and tannins. Most of these constituents are known to have inhibitive action. It is thereforeexpected that these compounds would exert a retarding action on the dissolution of base metals and would find applications in the acid pickling of composite systems [5]. So organic compounds in natural products having hetero atoms are found to have higher basicity and electron density and this assists in corrosion inhibition. Due to the bio-degradability, ecofriendly, cost-effectiveness, less-toxicity and easy availability of these products, the trend of using them have become increasingly important in the recent years [6]. Present study focused on removing the scale without metal weight loss by using waste material that we come across our day to day life. The important constituents present in carica papaya fruits (ripe and unripe) are sterols, teriterpenes, carbohydrates, glycosides, alkaloids, sapponin, pectin and tannins [7]. The alkaloid carpaine was isolated in pure crystalline form. The fatty acids, myristic, palmitic, steric, oleic, linoleic, lauric, 4 - methyl acetophenone, benzyl isothiocyanate, phenyl acetonitrole and myristoleic acids were detected in leaves, flowers and fruits [8-9], which expected to provide high inhibition to metal dissolution in acidic solution.

2. Material and Methods

A. Selection and Preparation of Metal

For present study, metal selected was mild steel (MS) due to its wide use in industrial purposes, low cost and easy availability, and also has high tensile strength than cast iron, but suffers from severe corrosion in acid environment and more dissolution during pickling process. The locally produced mild steel (rectangular steel sheet) was cut into pieces of 5 cm x 1cm area which had a percent nominal composition as measured by vacuum emission spectrometer DV-4, in PRICOL, Coimbatore, Tamil Nadu, India (% of C -0.06, Mn - 0.4, Si- 0.05, P- 0.03, S- 0.0277, Cr- 0.022, Mo- 0.014 and Ni- 0.0117). The specimen was polished to a smooth surface using different grade emery papers (No. 1/0 and 4/0) and degreed with CLARKS solution (50g of stannous chloride + 20g of antimony trioxide in 1000mL of conc. HCl).

B. Selection of Medium

HCl/ $H_2SO_4$is widely used for pickling, descaling and chemical cleaning process of steel and its alloys. Hence these medium were selected to study the inhibitive effect of carica papaya (C.P) on corrosion of MS.

C. Preparation of the Inhibitor

The C .P unriped fruits were collected, air dried under controlled conditions (shadow drying) to avoid too many chemical changes occurring. 5% extracts were prepared from 25g powder of each plant materials in 500 mL of 1M HCl/0.5M H_2SO_4 and refluxed for three hours, then kept over -night. The next day, the filtrate volume was made upto 500 mL using the same acid. HCl and H_2SO_4 -AR grade, antimony trioxide and Tin chloride- LR grade were used.

D. Characterization

1) FTIR

The inhibitor extract which was allowed to evaporate moisture, and dry powder was characterized by FTIR (Shimadzu, Japan) to observe functional group present and identify structure of the major constituents present in the prepared inhibitor molecule. Homogenous mixture of sample in KBr was prepared by grinding in mortar and by the action of 12 ton lab press to diminish moisture present in the sample. The spectra recorded for the sample for data accumulation in the range of 4000-600cm^{-1} at the spectral resolution of 4.0cm^{-1}.

2) XRD

X ray powder diffraction (XRD) patterns were recorded using Rigaku Model Ultima IV instrument with Cu K alpha radiation (Philips, Eindhoven, The Netherlands) using the dry mass of the extract. A spectrum was plotted between intensity and 2θ values, where it could identify the phase of the papaya extract used and could provide the cell dimensions of the material being analyzed. The average grain size was estimated by using Scherrer's formula,

$$d= (K\lambda) / (FWHM. \cos \theta) \quad (1)$$

Where, K-constant (0.94), λ- x-ray wavelength (0.15418nm), FWHM- full width half maximum in radians, θ-Bragg peak radians.

3) Zeta potential

Zeta potential of C.P extract was measured using Zeta Potential analyzer (Zetasizer Ver. 6.32, USA) at room temperature in the count rate of 15.6 kcps in the measurement position of 4.65mm for the duration of 1/2hr. The particle suspension was diluted with 0.1μL deionised water. Zeta potential was used to identify the mobility of the particle under magnetic field. Zeta potential depends on size and stability of the particle. This value was used to measure surface charge and stability of dispersion of particles in extract and electrolyte solution.

E. Surface Analysis

1) Contact Angle

The contact angle (C.A) was recorded between water droplet and metal surface after being treated with extract using the instrument HO-IAD-CAM 01 and photograph could represent the surface tension or surface energy of the metal. Drop shape analyzer was used to measure the wet ability of the MS surface by liquid (water) by Sessile drop method. Interfacial tension (IFT) measured based on the analysis of drop shape of pendant drop. Analysis of real and imaginary part of the interfacial dilation modulus was carried based on relaxing contour of pendant drop, a degree though which water spread on metal surface when it comes into contact with it. The measured IFT values were used to find the work of adhesion and measure the strength of contact between solid-liquid phases. More the IFT value more will be the work of adhesion, the surface being hydrophobic in nature [10]. If the C.A values between 0-45^o complete wetting, (the passive film due to adsorbed inhibitor molecule is hydrophilic), 45-90^o– good wetting (partially hydrophilic), above 120-bad-wetting (the inhibitor adsorbed metal surface is hydrophobic) [11]. According to Young's equation, relationship between CA (θ) and surface tension of liquid- σ_l, IFT- σ_{sl} between liquid and solid is calculated by

$$\text{Free Energy}= \sigma_{sl}+ \sigma_l \cos\theta \quad (2)$$

More IFT, more will be the free energy, more repulsive force, less corrosion.

2) FESEM

FESEM (Field Emission Scanning Electron Microscope) was used to study the surface morphologies of the MS specimen after exposed for 24Hrs in 0.5% C.P extract in 1M HCl medium by using ZEISS SIGMA instrument, Japan with a voltage from 0.5 to 30 kV.

3) EDAX

Energy dispersive X ray spectroscopy (EDAX) was used to study the elemental analysis or the chemical constituents present within the sample using ZEISS SIGMA instrument, Japan. It represents the sample image and hence the constituents present with respect to its concentrations using a peak with its X axis ranging from 0-16 keV. MS specimen used for this study was exposed in 1M HCl in the presence of 0.5% C.P extract for the period of 24Hrs.

F. Weight Loss Method

Test specimens of known area were weighed and three specimen were immersed in 100mL of 1M HCl / 0.5M H_2SO_4 acid / [acid + inhibitor] solution for a time of 1/2 Hr , 1Hr , 3Hrs ,6Hrs ,12 Hrs ,24Hrs to carry out the experiments in triplicates. They were taken out and washed thoroughly with tap water, rinsed with distilled water, dried and reweighed. The difference in weight gives weight loss (WL). The experiment was carried out in room temperature and at elevated temperature of 313K, 323K, 333K and 343K for varying concentration (from 0.05% to 0.7%).The corrosion rate (in mils per year-mpy), inhibition efficiency (I.E) and surface coverage (θ) in every case was calculated by using the formula:

$$C.R = (534 \times WL)/ (DAT) \quad (3)$$

$$I.E= (WL_O– WL) /WL_O * 100 \quad (4)$$

$$\theta= (WL_O– WL) /WL_O * 100 \quad (5)$$

Where, WL &WL$_o$ - weight loss with &without inhibitor (mg),D - density of mild steel (7.9 g /cc),A - area of the specimen (cm^2), T - exposure time (hrs).

G. Polarization Techniques

1) Tafel and Linear Polarization Techniques

The potentiodynamic polaraization studies of the specimen were measured using a three electrode SOLATRON 1280B electrometer to measures the Impedance, linear polarization and Tafel polarization. In a 100 mL beaker, 100 mL of 1M HCl/0.5M H_2SO_4 is taken, then a polished electrode (mild steel with diameter 1" x 1") is introduced and held for 30 minutes to attain a constant potential. The platinum electrode is placed at +400 mV cathodic to its open circuit potential (OCP). Then the potential is scanned at 1 mV/s towards the anodic direction. Tafel plot can be performed on a sample by polarizing the sample about 300mV anodically with the potential scan rate can be 0.1-1.0 mV/s. The resulting current is plotted on a logarithmic scale. The corrosion potential (E_{corr}), corrosion current (i_{corr}), Tafel anodic (b_a) and cathodic (b_c) slope is obtained from a Tafel plot by extrapolation of the linear portion of the curve to E_{corr}. CR calculated using the following equation:

$$C.R\ (mpy) = (0.13 \times I_{corr} \times Eq.\ Wt) / D \tag{6}$$

Where, i_{corr} is the corrosion current in µA.cm^{-2}, Eq. Wt is the equivalent weight of the corroding metal, D - is the density of the metal in gm cm^{-3}.The linear polarization resistant (LPR) and impedance (Nyqist plot) studies were also carried out using same instrument. Hence, 0.5% C.P extract was identified as optimum concentration to provide maximum efficiency, for further all studies (Tafel, LPR, Nyquist, C.A, EDAX, FESEM, and zeta potential) same concentration was used.

2. Impedance measurements (Nuquist plot)

Impedance measurements were carried out at each corrosion potential of an AC sine wave of 10 mV amplitude applied to the electrode with the frequency of 10 KHz to 100 MHz was super imposed at the OCP. The results are presented in the form of Nyquist plot. In this method the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) is obtained from the plots of Z' (real parts) vs Z" (imaginary part).

H. Adsorption Isotherm

The Langmuir isotherm (Plots Log θ/(1-θ) vs log Conc.) and Temkin isotherm (Plots θ vs log Conc.) were used to explain about the adsorption of inhibitors on metal surface. These adsorption isotherms appear to be the best descriptors to understand the mechanism of the interaction of inhibitor molecule with metal. If it yields a straight line with regression coefficient close to unity, it clearly indicates that the adsorption of the molecules from acidic solution on metal surface obey Temkin adsorption isotherm and Langmuir is other, indicating mono layer adsorption.

I. Corrosion Kinetic

1) Activation Energy (E_a) and Change in Free Energy (ΔG_a) of Adsorption

The activation energy (E_a) and change in free energy of adsorption (ΔG_a) at different concentration of the inhibitors at various temperature used was determined by plotting log C.R vs 1/T from the slope the E_a & ΔG_a was calculated using the formula:

$$E_a = 2.303 \times R \times slope \tag{7}$$

$$\Delta G_a = -2.303 \times R\ (T_2-T_1)\ Log\ K_2 / K_1 \tag{8}$$

Where, R -gas constant, T_1& T_2 -room temperature and higher temperature in Kelvin, K_1& K_2 are corrosion rate at T_1 and T_2 respectively. A plot of ΔG_a vs 1/Temperature was drawn. According to Gibbs - Helmholtz relation, $\Delta G = \Delta H - T\Delta S$, the slope of these lines are equal to enthalpy (ΔH) and intercepts corresponds to entropy ΔS of adsorption.

3. Results and Discussions

A. Characterization

1) FTIR

FTIR spectrum of inhibitor results is presented in fig. 1 Peak at 776.38, 1058.97, 1413.88, 1639.56, 2938.68, and 3446.94cm^{-1} is attributed to the C-H stretching (meta substitution), C-O stretching, C-H bending, C=C stretching, C-H asymmetrical stretching of CH_3 group, N-H and O-H stretching vibration respectively. These results reveal the presence of a functional group with lone pair of electron, which helps the adsorption of the molecule on metal surface [12-13]. The functional groups identified from this result coincide with phytochemical studies of major constituent functional groups such as linalool, benzyl isothiocyanate, phenylacetonitrile, 4-methyl acetophenone[15].

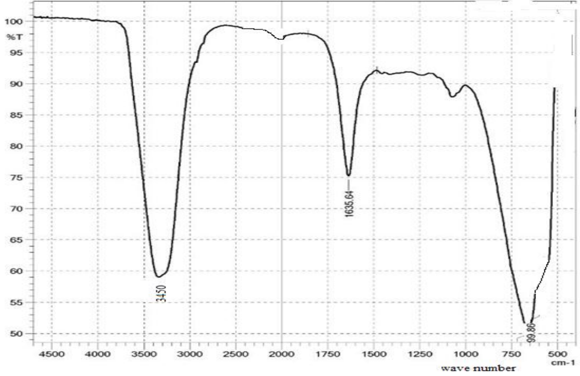


Fig. 1: FTIR absorption spectra of C.P

2) XRD

XRD peaks for the C.P. extract is presented if fig. 2 The peak values at 2θ are found, 29.11, 40.48, 44.07, 53.01, 81.80 and 88.46 assigned for the plan of 101, 111, 111, 200, 311 and 200 respectively, indicating that the extract contain polycrystalline constituents. The average grain size was estimated by using Scherrer’s formula, is 4.8nm.

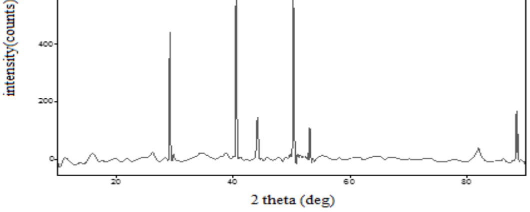


Fig. 2: XRD spectra of C.P

3) Zeta Potential

The stability and dispersibility of C. P constituent particle were estimated using zeta potential measurement and presented in fig. 3. The surface potential of C.P extracts are -7.7 and -92.6 eV and average particle dispersion size of 650d.nm. The increase in negative charge and smaller size of the particle distribution are due to the highly negative surface, which reflects the high stability and aggregation of particles on it because of repulsion force between adjacent molecules. If zeta potential takes a cross value around zero, the repulsive force between particles becomes weak and the particles will eventually aggregate bur our data showed a shift away from a zero point, higher levels of oxidization, aggregation and increase the adhesion, and permeability of the inhibitor molecules on metal surface [15].

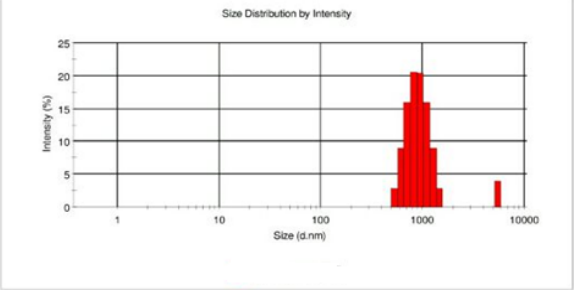


Fig. 3: Zeta potential spectra of C.P

B. Weight Loss Measurements

The role of acid extract of C.P. in 1M HCl and 0.5 M H_2SO_4 as determined on mild steel corrosion at room temperature by the weight loss method are given in fig. 4 (a& b). C.R and I.E of C.P was determined at different concentration (0.1% to 0.7%) with varying the time of immersion and at different temperatures. The C.R through the weight loss method decreases with increasing the concentration of C.P. extracts in 1M HCl as well as 0.5M H_2SO_4upto 0.5%, after that the corrosion rate is increased steadily. So the corrosion rate and the concentration are inversely related at low concentration, which indicates that the I.E was maximum at higher concentration of the extract. 0.5% was the optimum concentration at which the minimum C.R of 23.40mpy in H_2SO_4 and 114.87mpy in 1M HCl was noted in 6hrs duration. This is may be due to the highly corrosive nature of HCl. Fig. 5 (a & b) explains the relationship between the I.E and period of immersion in 1M HCl and 0.5M H_2SO_4 respectively. The I.E and the time of immersion are found to be directly proportional to each other. However, the maximum efficiency of 94.63% at 12 hrs and 92.20% at 24 Hrs was noted in 1M HCl from fig. 5a. Similar trend was observed as given in Fig. 5b. when the acid bath was 0.5M H_2SO_4. In case of H_2SO_4 bath, maximum efficiency of 98.7% was observed at 6hrs and at 12hrs the I.E was found to be 97.7%. The increase of I.E with immersion time indicates that the stability and persistence of the inhibitor film on the metal surface for upto 24Hrs.

Naturally occurring substances are found to be promising inhibitors and they prove to be temperature resistant. It can be suitably recommended for boiling systems. From table I it is clear that the inhibitor under study was temperature resistant and minimum C.R of 353.66mpy in 1M HCl and 1613.55mpy in 0.5M H_2SO_4 or maximum efficiency was obtained at 333K (93.01%) in 1M HCl and 95.67% in 0.5M H_2SO_4 at the optimum concentration of 0.5%. The Critical Micellar Concentration (C.M.C) was observed to be 0.4% to 0.6% at 323K (93.01%) and 333K (95.67%). The decrease in inhibitor efficiency after 333^0K may be due to desorption of inhibitor molecule from the metal surface at a faster rate at higher temperature. [16] So the plant extract in both acid medium could act as temperature resistant inhibitor upto 333^0K.

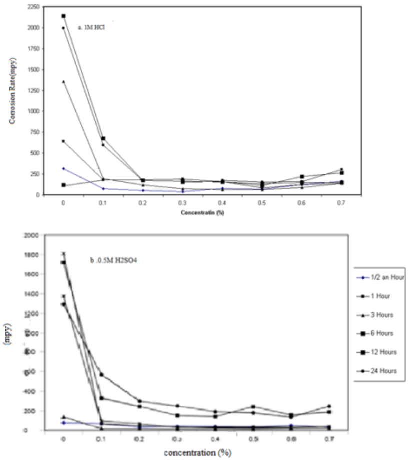


Fig. 4(a&b): Role of C.R on Con. Of 0.5%C.P in (a)1MHCl and 0.5M H_2SO_4

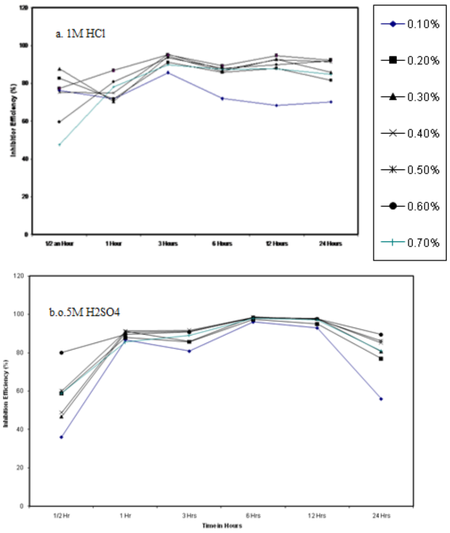


Fig. 5: Variation of I. E with time for C.P in (a) 1M HCl and 0.5M H_2SO_4

Table I: Relationship between C.R and Temperature (C.P. in 1M HCl and 0.5M H_2SO_4)

Conc. of C.P (%)	Temperature (K)									
	303		313		323		333		343	
	C.R (mpy)		C.R (mpy)		C.R (mpy)		C.R (mpy)		C.R (mpy)	
	1M HCl	0.5M H_2SO_4	1M HCl	0.5M H_2SO_4	1M HCl	0.5M H_2SO_4	1M HCl	0.5M H_2SO_4	1M HCl	0.5M H_2SO_4
Blank	315.73	78.49	4301.42	3183.49	3738.64	10720.08	14474.86	15853.79	24375.52	22151.88
0.1	75.00	69.77	876.98	594.83	3221.86	1679.83	3018.21	3450.38	5126.72	5157.25
0.2	54.94	32.27	1730.42	413.41	2076.68	1412.49	4026.02	2239.78	3499.65	4690.63
0.3	39.24	41.86	842.53	310.49	1716.41	1132.97	1943.23	1949.34	5492.17	3355.31
0.4	78.00	40.12	1227.16	259.04	507.68	933.24	1630.11	1613.55	5566.77	2776.18
0.5	71.74	31.39	950.25	329.68	353.66	936.73	1050.54	1951.08	4223.57	2014.75
0.6	127.62	15.69	820.25	305.26	1557.09	842.53	1105.50	2276.41	3777.88	2514.52
0.7	165.81	32.27	950.38	366.31	2117.67	839.61	1422.97	2369.74	4311.43	2745.65

C. Potentiodynamic Polarization Studies

1) Tafel and LPR Studies

From the weight loss experimental results, the optimum concentration for maximum I.E was confirmed at 0.5% and polarization studies had been carried out for that concentration.

Potentiodynamic Polarization curves for C.P. in 1M HCl and 0.5M H_2SO_4 are illustrated in the fig. 6 (a & b) respectively and the corrosion parameters deduced from Tafel polarization such as I_{corr}, E_{corr} and Tafel constants b_a &b_c and LPR values are tabulated in the II & III. Inhibitor values obtained from these studies (I_{corr} and E_{corr}) values and weight loss method reports for different composition of the compounds under study could show good agreement in both acid medium. This observation may be due to the formation of a thick inherent and continuous film on the metal surface [17]. This leads to the complete shielding of the metal surface from the corrosion environment. The I_{corr} values decrease considerably in the presence of inhibitor. This shows that the inhibitor under study could perform inhibitive action. The change in b_a and b_c values with respect to the blank values indicated, the compound as mixed inhibitors. Maximum inhibition efficiency in the polarization technique may be due to the adsorbed inhibitor may cover the entire metal surface but occupies the sites, which are electrochemically active and there by reduces the extent of anodic and cathodic reaction i. e. mixed type inhibitor [18].

2) Impedance Studies

Fig. 7 (a&b) and table IV depicted impedance (Nyquist) measurements plot, which consists of the values of potential resistance (R_{ct}) and C_{dl} for mild steel in 1M HCl and 0.5M H_2SO_4 for uninhibited and inhibited systems. High I.E in 1M HCl may be due to the adsorption of the inhibitor molecules on metal surface. It can be seen that the impedance spectra are not semi circle for 0.5M H_2SO_4. The depressed semi circle and more corrosion is due to the presence of pores on the electrode surface. The negative I.E values for sulphuric acid may be due to the weight loss method conducted for an extended time, whereas polarization studies are experiments of short duration and time will not be enough for the formation of the continuous film. This leads to the low values of inhibitor efficiency in H_2SO_4 bath [19]. These electrochemical results reflected that the inhibitors under study behaved as a mixed one interfering with the electrode reaction both at anode as well as at cathode. Corrosion rate will be decreased in proportion to the extent to which the electrochemically active sites are blocked by the adsorbed inhibitor and there by decrease the corrosion rate of the metal surface [20].

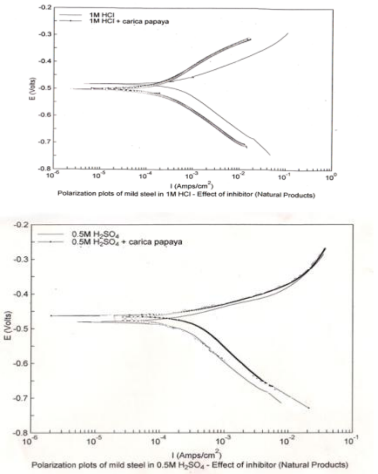
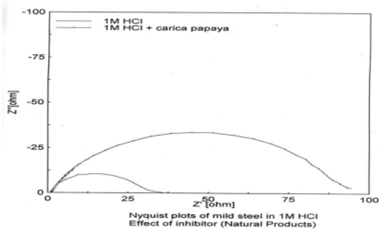


Fig. 6(a&b): Tafel plot for MS in the presence of 0.5% C.P in (a) 1M HCl and 0.5M H_2SO_4



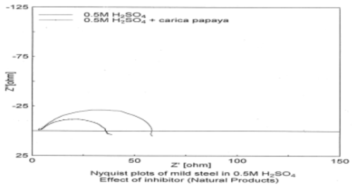


Fig. 7: Nyquist plot for MS in (a) 1M HCl and (b) 0.5M H_2SO_4 in the presence of 0.5% C.P

Table II: Electrochemical Corrosion Studies Parameters for MS in the Presence of0.5%C.P Extracts (Tafel Plot)

S.No	Inhibitor	$-E_{Corr}$ mV/SCE	I_{corr} mA/cm^2 x 10^{-4}	Tafel constants mV / dec.		I.E (%)
				b_a	b_c	
1	Blank 1M HCl	482	53	74	128	-
2	0.5% C.P.	500	1.77	100	115	96.66
3	Blank 0.5M H_2SO_4	480	53.35	95	165	-
4	0.5% C.P.	471	1.55	72	118	97.09

Table III: Linear Polarization Resistant Studies Results of MS in 0.5% C.P Extract

S.No	Inhibitor	R_p ohm. cm^2	I_{corr} mA/cm^2 x 10^{-4}	I.E (%)
1	Blank 1M HCl	32.6	0.624	-
2	0.5% C.P.	71.6	0.324	48.06
3	Blank 0.5M H_2SO_4	53.72	0.723	-
4	0.5%C.P.	32.52	0.437	39.56

Table IV: Impedance Studies Parameters of MS in 0.5% C.P Extract (Nyquist)

S.No	Inhibitor	$-E_{Corr}$ mV/SCE	R_P ohm. cm^2	$I_{Corr.}$ mA. cm^2	I.E (%)
1	Blank 1M HCl	482	190	0.107	-
2	0.5% C.P.	500	133	2.436x 10^{-3}	97.72
3	Blank 0.5M H_2SO_4	480	81.6	0.2984	-
4	0.5% C.P.	471	62.43	0.311	-4.22

D. Adsorption Isotherms

Efforts had been taken to study a suitable adsorption isotherm for the corrosion inhibition of plant material under study. Adsorption isotherms such as Langmuir and Temkin had been tried. Results calculated from values of θ obtained at various concentrations of the plant material extracts by weight loss method and presented in fig. 8(a& b) that indicate it follows Langmuir adsorption. Further examination of the data revealed that when θ was rather small, the adsorption isotherm of the plant materials followed Temkin equation [21]. Our data reflected that when θ is smaller, the interaction among adsorbed molecules can be neglected and the behavior of adsorption is affected by the heterogeneity of the electrode surface. Fig. 9(a&b) Temkin isotherm is applicable to this case.

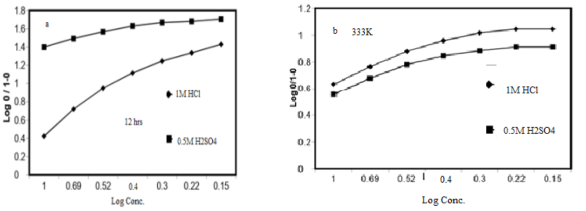


Fig. 8: Langmuir adsorption isotherm for MS in 0.5% C.P in 1M HCl and 0.5M H_2SO_4at (a) room temperature (12hrs) and (b) at 333K

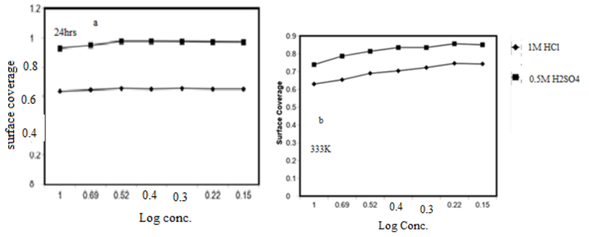


Fig. 9: Temkin adsorption isotherm for MS in 0.5% C.P in 1M HCl and 0.5M H_2SO_4 at (a) room temperature (12hrs) and (b) at 333K

E. Corrosion kinetics

1) Activation Energy (Arrhenius Parameters)

To evaluate a suitable mechanism for the plant extracts under study, the values of E_a, ΔG_a, ΔH_a and ΔS_a are calculated and presented in table V (a&b). The activation energy was calculated for this reaction from the plot of log C.R vs 1/Temperature and presented in fig. 10, from the slope values E_a obtained. The activation energy values of the inhibited system was found to be lower than those of blank system, which indicated the chemical adsorption taking place on metal surface, if the activation energy for chemical adsorption is greater than 80KCal/mole and less than this value for physical adsorption mechanism [22]. The high values of activation energy in the present work indicated that the probable inhibition made by the plant extract might be through chemical adsorption. The low and negative values of free energy were obtained illustrating that there was a spontaneous adsorption of the inhibitor on the surface of the mild steel. The increase in the free energy of adsorption with increase in temperature suggest that the chemical adsorption of the inhibitors on the surface of the mild steel. Physical adsorption may be involved at lower concentrations, but at higher concentration, a contribution of chemical adsorption can be included, since the inhibitor efficiency increases with increasing temperature [23- 24].

2) Free Energy

Fig. 11 gives us relationship between free energy change (ΔG) and temperature. Using Gibbs-Hemholtz equation, the slope of the plot is equal to Entropy Change (ΔS) and intercept of free energy change (ΔG) axis gives the corresponding heat of adsorption (ΔH). When the concentration of the inhibitor increased, ΔH and ΔS decreased upto C.M.C. after whichΔH &ΔS increased slightly. This may be due to the fact that adsorption is an exothermic process and is always accompanied by a decrease of entropy [25]. Therefore, the gain in entropy that accompanies the substitutional adsorption process is attributed to the increase in solvent entropy.

Table V.a: Determination of E_a and Thermodynamic Parameters (C. P.) in 1M HCl on MS

Conc. of C. P (%)	E_a Kcal. / mole	(-)ΔG_a Kcal. / mole				(-)ΔH Kcal. / mole	(-) ΔS Kcal. /mole. deg.
		313K	323K	333K	343K		
Blank	19681.37	51.90	2.78	26.90	10.35	94970	268.06
0.1	19242.08	45.76	25.86	1.29	10.53	130260	376.43
0.2	18194.17	68.56	3.62	13.15	2.78	187810	550.79
0.3	21264.67	60.94	14.14	2.46	20.64	132900	380.88
0.4	17526.08	54.76	17.54	23.18	24.40	85440	230.62
0.5	17736.57	51.38	15.53	19.92	27.63	66860	175.30
0.6	14066.62	36.97	12.73	6.80	24.42	43580	112.68
0.7	13755.45	34.69	15.92	7.90	22.03	46000	120.16

Table V. b: Determination of E_a and Thermodynamic Parameters (C. P.) in 1M 0.5M H_2S0_4 on MS

Conc. of C.P %	E_a Kcal./ mole	(-)ΔG_a Kcal. / mole				(-)ΔH Kcal./ mole	(-) ΔS Kcal./mole. deg.
		313K	323K	333K	343K		
Blank	25621.02	57.9	22.12	1.15	8.97	15476	446.23
0.1	20596.57	42.58	20.63	14.30	7.98	110130	314.52
0.2	23154.56	50.68	24.42	9.15	14.69	132492	377.05
0.3	21072.48	39.82	25.72	10.78	10.79	102030	289.41
0.4	20473.02	37.06	25.47	10.88	10.78	93430	263.91
0.5	15375.36	46.73	20.75	10.01	5.20	130184	377.67
0.6	24165.85	58.98	20.17	19.66	2.06	171270	497.15
0.7	21374.49	48.27	16.48	20.62	2.92	131910	380.25

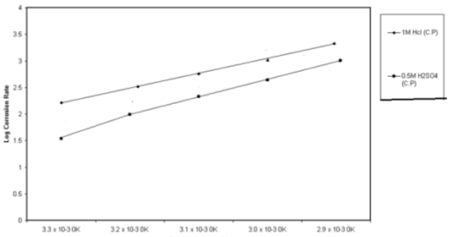


Fig. 10: Arrhenius plot for 0.5% C.P. in acid medium

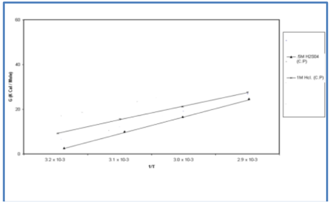


Fig. 11: Temperature dependence of the free energy of adsorption

F. Surface Analysis

1) FESEM

FESEM micrograph of MS fresh specimen and exposed specimen in 1% HCl in the presence of 0.5% C.P extract for the period of 24Hrs at 25^0C was carried out in the magnification of 3000X are compared in fig. 12 (a& b) respectively. It identify clearly that the chemical constituents which, present in C. P extract are present on metal surface. It shows that the inhibitor molecule on metal surface is present in the form of an amorphous, and spherical with rough texture.

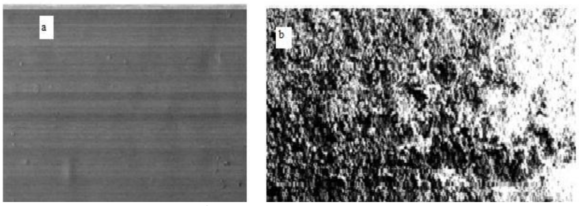


Fig. 12: FESEM images of mild steel (a) Fresh specimen(b) exposed in 0.5% C. P in 1%HCl for 24hrs at $25^{0}C$

2) EDAX

Fig. 13(a, b) shows EDAX results obtained for MS surface after treated with 1% HCl + 0.5% C.P extract for 24hrs at $25^{0}C$ and its elemental composition. It is seen that elements of C, O, N, S, Cl & Fe are identified, where the elements Cl& Fe are from 1% HCl acid medium and MS respectively. It is comparable to the major constituents present in C.P fruit skin with phytochemical studies of linalool, benzyl isothiocyanate, phenyl acetonitrile, 4-methylacetophenone [8]. The high corrosion I.E effect of C.P extract is may be due to lone pair e^- present on hetero atoms. The elemental composition of EDAX result is compared to the composition of major constituents present in the inhibitor; there is an obvious increase in I.E in both acid medium due to synergistic effect [26].

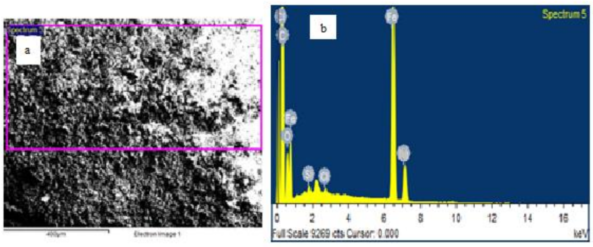


Fig. 13: EDAX images of mild steel (a) Exposed in 0.5% C. P in 1% HCl, (b) Elemental composition for 24hrs at $25^{0}C$

3) Contact Angle

Contact angle of C. P extract coated & water by sessile drop method was carried out at room temperature to find wetting property of adsorbed inhibitor molecule on MS. Water drop immediately spread on MS surface, are the surface is hydrophilic in nature. The contact angle is 8.5 to 9.4 ^{o} only with interfacial tension (IFT) 0.048 and 0.090 mN/ m [27].

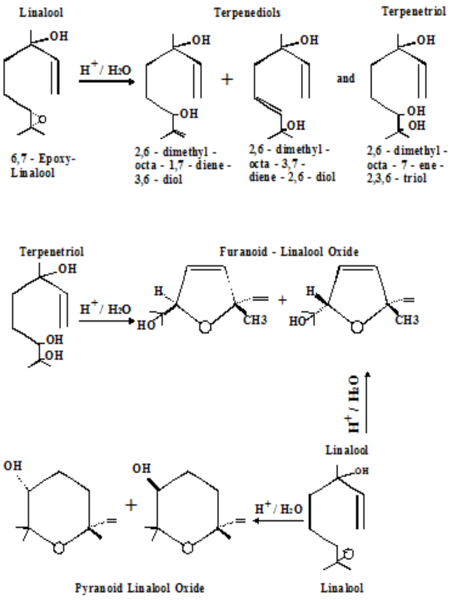
Fig. 14: Contact angle photograph of water droplet on MS after exposed in 10% C.P and 1% HCl

G. Correlation of Corrosion Inhibition, Molecular Structure and Mechanism

In acid media the corrosion inhibition offered by the extracts of C.P. for mild steel was investigated and the inhibition may be due to inhibitor molecules adsorbed on the metal surface. A correlation between inhibition and electronic configuration of the molecule was attempted. The performance of an organic inhibitor is related to their chemical structure and physiochemical properties of the compound. The plant extracts were found to follow Langmuir and Temkin adsorption isotherms (i.e.) they inhibit corrosion by an adsorption mechanism. In this case of corrosion of metal in acid solution, adsorption of inhibitor due to electrostatic forces (Vander Waals) and metal chemisoption are important in inhibition.

The extracts of the examined plant materials contain N, O and S containing organic compounds. The free electrons in these atoms form bonds with electrons on the metal surface. Thus a single molecule attaches itself to the metal surface at several places. When the inhibitor is added to a solution, particularly an acidic solution, inhibitor species may become unstable and give rise to a new species due to decomposition. The inhibition due to the action of the initially added inhibitor is known as primary inhibition and the inhibition due to the reaction product is known as secondary inhibition. As reported by Peter Winter Halter, et al., (1986) C.P. acid extracts gives the following components [8]. Very high values of inhibition efficiency for these compounds were understandable from the number of anchoring atoms and groups present in the molecule. The molecular structure of all the compounds had an extensively delocalized orbital filled with a number of π e- contributed from the different anchoring atoms of the molecule [28]. It was expected from the molecular structure that these molecules might be adsorbed on the metal surface through oxygen atoms in acidic solution, hydrogen permeation in metals take place. More over these compounds may also form complexes with metallic cations. These complexes can causes blocking of the micro anodes and/or the micro cathodes that are generated on the metal surface. Thus a single molecule attaches itself to the metal surface at several places. The bonds can be formed due to the interaction between the π e- on the ring and oxygen atoms with the positively charged iron metal surface (with vacant 'd' orbital), resulting in the adsorption of the compound on the metal surface [29]. The electrostatic interaction of the positively charged cations formed in acidic solution by its combination with hydrogen ion, with negatively charged metal surface may also be responsible for the adsorption of this compound on the surface.

According to Peter Winter Halter, et al., (1986) following structural modification taking place in the carica papaya chemical constituents in acid medium:



4. Conclusion

Naturally occurring compounds could act as an environmentally friendly and non-toxic inhibitors. These non-toxic inhibitors formulation are essential to replace the toxic inhibitors and will reduce the environmental pollution. Efforts have been taken to study the beneficial role of inhibitive action of the acid extract Carica Papaya (Fruits) on mild steel in 1% HCl and 0.5% H_2SO_4 by classical weight loss method and potentiodynamic methods. The investigated plant material (C.P.) is an effective inhibitor for the corrosion of mild steel in 1M HCl and 0.5M H_2SO_4. Critical Miceller Concentration was found to be 0.5% for C.P. at room temperature in 1M HCl and 0.5M H_2SO_4. The investigated inhibitors proved to be temperature resistant. Arrhenius parameter could reflect that the mechanism of inhibition as chemical adsorption. The values of Ea, ΔG, ΔH and ΔS could predict a suitable mechanism involving chemical adsorption. Langmuir adsorption isotherm could be effectively followed by the inhibitor under study and reflected a mono layer formation. Temkin adsorption isotherm may also be recommended indicating heterogeneity of the electrode surface. Potentiodynamic studies were carried out and comparable results are obtained by Tafel, Linear and impedance techniques, results reflected that the inhibitor under study behaved as mixed one, interfering with the electrode reaction, both at anode as well as cathode.

Acknowledgement

The authors would like to thank Amrita Vishwa Vidyapeetham, Bio sensor lab staffs and Chemistry department staffs Coimbatore campus, Tamil Nadu, India, for their support to carry out this work. We are indebted to Dr. S. Subhashini, Department of Chemistry, Avinashilingham Deemed University, Coimbatore, Tamil Nadu, India for permitting and guiding to do these studies.

References

[1] Shen Ming Chen B, Karthik, R, Muthukrishnan P, Jayaprabha B & Prakash P, "Anticorrosion inhibition of mild steel by using Tiliacoraaccuminata leaves extract", *Int. J. Electrochem. Sci.*, Vol.10, (2015), pp.3707-3725.

[2] Zhang DQ, Gao LX & Zhou GD, "Study of mechanism of corrosion using VCI papers", *Corrosion.*, Vol.61, No.4,(2005),pp.390-392.

[3] Miksic BA & Miller RH, "Fundamental Principles of Corrosion Protection with VPI", *5th European Symposium on Corrosion Inhibitors, European Federation of Corrosion*, (1980).

[4] Sastri VS & Perumaredi JR, "Corrosion inhibition by substituted Toludine", *Corr. J.*, Vol.53, (1997), pp.201-209.

[5] Saleh RM, Ismail AA & El.Hosary AA, "Corrosion inhibition by naturally occuring substances on mild steel, Aluminium, Zinc and Copper in acid medium", *Corr. Prev. and Control*, Vol.30, No.2, (1984), pp.21-23.

[6] Poongothai N, Natesan M, Murugavel SC & Ramachandran T, "Essential Oils as VCI for mild steel in HCl environment", *Mat. Performance*, Vol.5, (2009), pp.52-57.

[7] Lynn KR, "Definition of the site of reactivity of the ancestral protease of the pappin type", *Phytochmistry*, Vol.22, No.11,(1983), pp.2485-2487.

[8] Winterhalter P, Katzenberger D & Schreier P, "6, 7-Epoxy-linalool and related oxygenated terpenoids from Carica papaya fruit", *Phytochemistry*, Vol.25, No.6,(1986), pp.1347-1350.

[9] Schwab W, Mahr C & Schreier P, "Studied on the enzymic hydrolysis of bound aroma compounds from Carica papaya Furits", *J. Agric. Food Chem.*, Vol.37, (1989), pp.1009-1012.

[10] Ayman M, Atla HA, Al-Hodan RS, Abdel Hameed & Essat AO, "Preparation of green cardinal based epoxy & hardener as primer coating for petroleum & gas steel in marine environment", *Progress in Org. Coatings.*, Vol.111, (2017), pp.283- 293.

[11] Prajitno DH, Maulana A & Syarif DG, "Effect of surface roughness on contact angle measurements of nano fluid on surface of stainless steel by sessile drop method", *6th Asian Physics symposium, IOP Publishing*, (2016).

[12] Silverstein RM, Clayton Bassler G, Terence C & Morrill C, "Spectroscopic identification of Organic Compounds", *John Wiley Sons*, (1991), pp.45-57.

[13] Poongothai N, Murugavel SC & Ramachandran T, "Corrosion Inhibitive Effect Of Five Essential Oils On Copper In Seawater, Rainwater, And Industrial Environments". *Int. J. Chemistry and Chemical Engineering*, (2014), pp.23-34.

[14] Hashem FM, Haggag MY & Galal AMS, "A Phyto Chemical study of Carica papaya", *Egypt, J.Pharm.Sci.*, Vol.21, No.3,(1983), pp.199-213.

[15] Giribaldi G, Ulliers D, Mannu F, Arese P & Turrini F, "Growth of Plasmodium falciparum induces stage-dependent haemichrome formation, oxidative aggregation of band 3, membrane deposition of complement and antibodies, and phagocytosis of parasitized erythrocytes", *British Journal of Haematology*, Vol.113, No.2, (2001), pp.492–499.

[16] Poongothai N, Murugavel SC, Natesan M & Ramachandran T, "Essential oils as vapour phase corrosion inhibitors for mild steel in seawater, rainwater, SO_2 and H_2S environments", *Mat. Perf. J*, (2010), pp.59-62.

[17] Rakanta E, Zafeiropoulou Th & Batis G, "Corrosion protection of steel with DMEA-based organic inhibitor", *Construction and Building Materials*, Vol.44, (2013), pp.507–513.

[18] Poongothai N, Natesan M, Palanisamy N, Murugavel SC & Ramachandran T, "Azole, amine and nitrite as vapour phase corrosion inhibitors of metals in NaCl& SO_2 environment", *Indian Journal of Chemical Technology*, Vol. 12, (2007), pp.427-431.

[19] Quraishi MA, Khan MAW, Ajmal M, Muralidharan S & Iyer S, "Influence of green compounds of corrosion inhibition on mild steel in NaCl", *Corrosion*, Vol.53, No.6, (1997), pp.475-80.

[20] Sing G, Jha L & Sing RR, "Halide in corrosion inhibition of mild stee", *J. Elec. Chem., Sco, India*, Vol.39, No.2,(1990), pp.70-75.

[21] Poongothai N, Rajendran P, Natesan M & Palaniswamy N, "Wood bark oil as vapour phase corrosion inhibitors of metals in NaCl& SO_2 environment", *Indian Journal of Chemical Technology*, Vol. 12, (2005), pp.641–647.

[22] Solmaz R, Kordas G, Culha M & Yazic B, "Investigation of adsorption and inhibitive effect of 2-mercapbutothioline on corrosion of mild steel in 1M HCl", *Electrochemical Acta*, Vol.53, (2008), pp.5941-5952.

[23] Solmaz R, "Investigation of inhibitive effect of 5-phenyl buta 1,3-dienyldeneamino 3,4 thiodiazolschiff base on mild steel corrosion in 1M HCl", *Corr. Sci*, Vol.52, (2010), pp.3321-3330.

[24] Saha SK, Dutta A, Ghose P, Sukul D & Banerjee P, "Novel Schiff base molecule as efficient corrosion inhibitor for mild steel in 1MHCl- Experimentl and theoretical approach", *Phys. Chem*, Vol.18, (2016), pp.17898-17911.

[25] Saha SK, Dutta A, Ghose P, Sukul D & Banerjee P, "Adsorption and corrosion inhibition effect of Schiff base on mild steel in 1M HCl", *Chem. Phys*, Vol.17, (2015), pp.5679-5690.

[26] Umoern S, Gobobe O & Ebeso E, "Inhibition of mild steel corrosion in acidic medium using synergistic naturally occurring polymers", *Corr. Sci.*, (2008), pp.1998-2006.

[27] Kundu CK, Wang W, Zhou S, Wang X & Hu Y, "A green approach to constructing multilayered nanocoating for flame retardant of polyamide 66 Fabric Chitosan and sodium alginate", *Carbohydrate polymers*, Vol.166, (2017), pp.131-138.

[28] Flath RA, Light DM, Jang EB, Richard Mon T & John JO, "Headspace examination of volatile emissions from ripening papaya", *J. Agri. Food Chem.*, Vol.38, (1990), pp.1060-1063.

[29] Poongothai N, Murugavel SC, Natesan M & Ramachandran T, "The Performance of VCI coated paper for corrosion prevention of copper in HCl environment", *International Journal of AsJRC*, Vol. 3, (2010), pp.54-59.