Adsorption and Thermodynamic studies of *Carica papaya* leaves extract (yellow) as Corrosion Inhibitor for mild steel in acidic medium

Abstract: The inhibitive effects of plant leaf, *Carica papaya* leaves extract (yellow), CPLE (yellow) was studied on mild steel in 1.0 M HCl solution at 30°C using the gravimetric, electrochemical methods and Fourier transform infrared spectroscopy, FT-IR technique. The analysis of spectra obtained from FT-IR revealed that some functional groups present in the original spectrum were missing in the spectra of the corrosion products, an indication of interaction between the mild steel and inhibitor. The corrosion rate decreases noticeably with increase in inhibitor concentrations, that is, the inhibition efficiency (% IE) increases with increase in the inhibitor concentration. The progressive increase of the extract shows greater reduction of corrosion rate, given maximum inhibitive efficiency of 94.68% at 0.5g L^{-1} at 30°C. The Tafel and potentiodynamic polarization studies revealed that the CPLE (yellow) functioned as mixed-type inhibitor. The adsorption mechanism of the extract on the mild steel surface was found to obey El-Awady isotherm model. The thermodynamic evaluation deduced proposed a physisorption with the mild steel surface and spontaneous adsorption of CPLE (yellow). FT-IR was used to confirm the formation of a protective layer on the mild steel surface.

***Keywords*:** Mild steel, CPLE (yellow), El – Awady isotherm, Adsorption, Thermodynamic

1. INTRODUCTION

The impact of corrosion of materials, particularly, metallic structures (e.g mild steel and aluminium) on the economy have continued to generate interest, not only among the scientific community, but globally. A substantial economic loss and sometimes, loss of lives are incurred by the industries concerned as a result of rapid corrosion of these structures, due to the aggressiveness of the acidic media involving pickling, chemical cleaning, oil-well acidizing and descaling among others [1, 2]. Unmitigated corrosion has the negative effects of causing rigidity weakening of mild steel based installations, thereby compromising the mechanical properties and ultimately, facility breakdown [3]. Among various techniques adopted to control this menace, corrosion inhibitors have proven excellently in regard to cost, availability, processing, and reproducibility. However, due to their high cost and stringent environmental laws, particularly because of health awareness and ecological risks, focus has continually drawn towards finding highly efficient, affordable and non-toxic inhibitors. The use of green corrosion inhibitors has continued to draw the attention of researchers due principally to their non-toxicity, environmental friendliness and good performance [4, 5].

The natural plant products as corrosion inhibitors have been utilized and proven to be good with higher prospect viz-a-viz the synthetic or chemical inhibitors. Plant – mediated corrosion inhibitors represent the advanced trends of managing corrosion based on green chemistry and research efforts are still ongoing to discover higher performance corrosion-inhibiting additives with optimum concentration [1, 6-8]. These green plants inhibitors molecules consist of heterocyclic compounds with polar functional groups such as O, N, S, P and π electrons with double rings [9]. However, specific areas that are crucial in regard to the nature of active constituents, the chemical structures of the extract and, the use of density functional theory to correlate the extract active components and inhibitive effects on the basis of the molecular parameters are still few and require further elucidation. In the present study, the investigation of *Carica papaya* leaves extract, CPLE, (yellow), on the inhibition of mild steel in 1M HCl acid solution is another attempt towards contributing to the growing interest of exploring green corrosion inhibitors. The aim of this research therefore, is the adsorption and corrosion inhibition of *Carica papaya* leaves extract, CPLE, (yellow), on mild steel in the presence of 1M HCl acid solution at room temperature (30^oC).

2. MATERIALS & METHODS

Commercially available mild steel was used for all experiments of average nominal composition; 98.3% Fe, 0.128% C, 0.010% P, 0.030% S, 0.820% Cr, 0.292% Mn, 0.115% Ni, 1.420% Ar, 0.092% Pb, 0.074% Cu and 0.066% N respectively. *Carica papaya* leaves extract (yellow), CPLE (yellow) is the inhibitor used. The *Carica papaya* leaves were sourced from the Federal Polytechnic Ado-Ekiti campus, Nigeria. The leaves samples were washed; oven dried at 90°C for 4 hours and pulverized using an electrically powered blender. About 50g of the pulverized leaves was weighed and soaked in 250ml of ethanol for 48 h. The solution of the sample was then filtered to obtain the extract. The filtrates were furthered subjected to evaporation at 352K to remove excess ethanol. CPLE (yellow) was prepared in volumetric concentration of 0.1, 0.2, 0.3, 0.4, 0.5g L^{-1} per 200ml of the acid solution respectively. Solution of 1.0M HCl of analytical grade was used as the corrosion test media. Mild steel specimen of the required size was used for measurement of weight loss study. The strips were mechanically polished using emery papers of grade numbers 220, 320, 400, 600, 800, and 1000; washed thoroughly with distilled water, degreased with acetone and dried in air before immersion in the corrosive medium.

The corrosion tests were carried out at 30^oC and the conditions under which they were done are as follows: the Fourier transform infrared spectroscopic, FTIR analysis of the *Carica papaya* leaves extract (yellow) and that of the corrosion products in the presence of the extracts were prepared utilizing Perkin-Elmer-1600 Fourier transform infra-red spectrophotometer. The corrosion product from the mild steel specimen for the analysis was obtained following the procedures in accordance with [3]. This entailed the immersion of the powdered mild steel inside 150ml of 0.5g CPLE (yellow) concentration. The mixture was left for 6hrs after which it was filtered. The residue was allowed to dry and then analyzed using FT-IR. The sample was prepared using KBr.

The weight loss measurements were carried out by weighing the specimens in triplicate before use and after immersion in 200ml for 24hrs in 1.0M HCl in the absence and presence of 0.1, 0.2, 0.3, 0.4, 0.5g/l of inhibitor CPLE (yellow) at 30^{o}C. Each of the test specimens was taken out every 24hrs, washed thoroughly with liquid soap (Morning fresh), rinsed with distilled water, cleaned with acetone, dried and re-weighed. The test was also carried out progressively for 168hrs (7days). The corrosion rate (CR), inhibition efficiency $(\% \, IE)$ and surface coverage (θ) were calculated from the following equations in accordance with ASTM G31 standard [10].

$$CR\ (mmpy) = \frac{87.6\,W}{DAT} \tag{1}$$

$$\%\,IE = 1 - \frac{CRinh}{CR\ blank} \times 100 \tag{2}$$

$$\theta = 1 - \frac{CR\,inh}{CR\,blank} \tag{3}$$

Where W is the weight loss in grammes, D is the density in g/cm^2, A is the surface area in cm^2, T is the immersion time in hrs, CR_{inh} and CR_{blank} are corrosion rates of mild steel with and without inhibitor respectively. The procedure was utilized for all the 168hrs (7days), using thermostat to study the inhibition efficiency of inhibitor. The study gives details about the rate of adsorption and thermodynamic parameters of the corrosion inhibition mechanism.

The electrochemical corrosion studies of mild steel in various concentration of *Carica papaya* leaves extract yellow (CPLE yellow) in 1 M HCl were carried out using AUTOLAB PGSTAT 204N instrument, piloted by Nova software. The electrochemical measurements were carried out in a three-electrode cell made up of the mild steel sample as the working electrode, while the saturated silver/silver chloride and platinum wire were utilized as reference and as counter electrodes respectively. The working electrode was immersed in test solutions 1M HCl solutions with or without *Carica papaya* leaves extract for 30 minutes until a stable open circuit potential was achieved. The working electrodes were prepared by attaching an insulated copper wire to one face of the sample using aluminium conducting tape and cold mounting it with epoxy resin. The potentiodynamic polarization measurements were carried out using a scan rate of 1.0 mV/s at a potential initiated at -250mV to +250mV with respect to OCP. After each experiment, the electrolyte and the test sample were replaced. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion densities (i^{o}_{corr} and i_{corr}) in place of corrosion rates (C^{o}_{R} and C_{R}) in Eq. (2).

3. Results & Discussions

3.1 FTIR Spectral Analysis of CPLE (Yellow)

FTIR characterization of the CPLE (yellow) was performed to identify the functional groups present in it, while that of the corrosion products is to ascertain that inhibition has taken place due to interaction/adsorption between the mild steel surface and the inhibition extract. The FT-IR spectra of the inhibitor extract and the corrosion products of the specimen are shown in Figures 1a and 1b. From the results obtained, the bonded O – H stretching in phenol 3389.52cm^{-1} was shifted to 3282.68cm^{-1}, C=O stretch of carbonyl at 1714.92 cm^{-1} was shifted to 1712.52 cm^{-1}, C-O stretch of ester at 1083.25 cm^{-1} was shifted to 1117.62 cm^{-1}, C=C stretch at 1454.44 cm^{-1} was shifted to 1462.36 cm^{-1}, N – O stretch of nitro molecule at 1376.59 cm^{-1} was shifted to 1377.00 cm^{-1} and the C-H stretch corresponding to carboxylic acid group at 2922.84 cm^{-1} was shifted to 2922.45 cm^{-1}. The shift in the frequencies indicates that there are significant changes between the metallic substrate and the inhibitor. Moreover, a band of 1103.13 cm^{-1} corresponding to C-O stretching of ether and Methyl C-H at 1462.36 cm^{-1} observed in the FT-IR spectral disappeared, suggesting that these bands must have been utilized in the adsorption of the inhibition extract onto the mild steel substrate [11-13]. These changes resulted in the formation of a protective film barrier on the mild steel substrate [14].

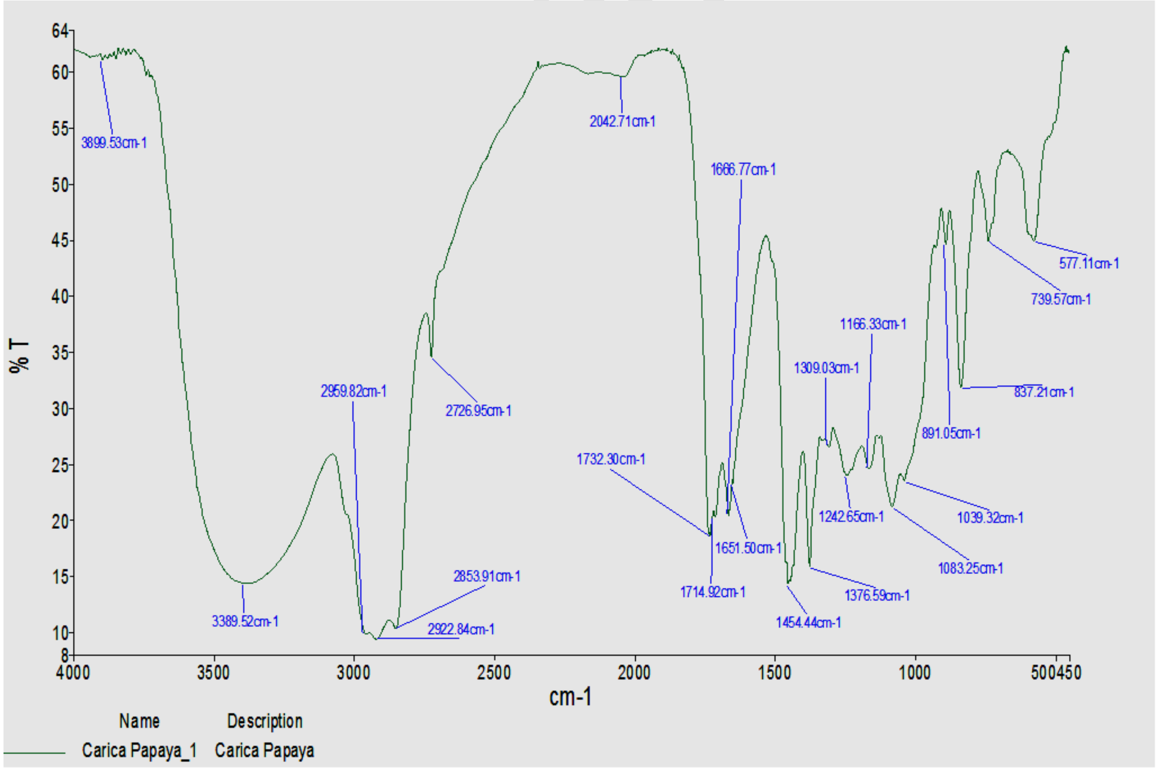

Fig. 1a: FT-IR spectrum of HCl extract of *Carica papaya* leaves

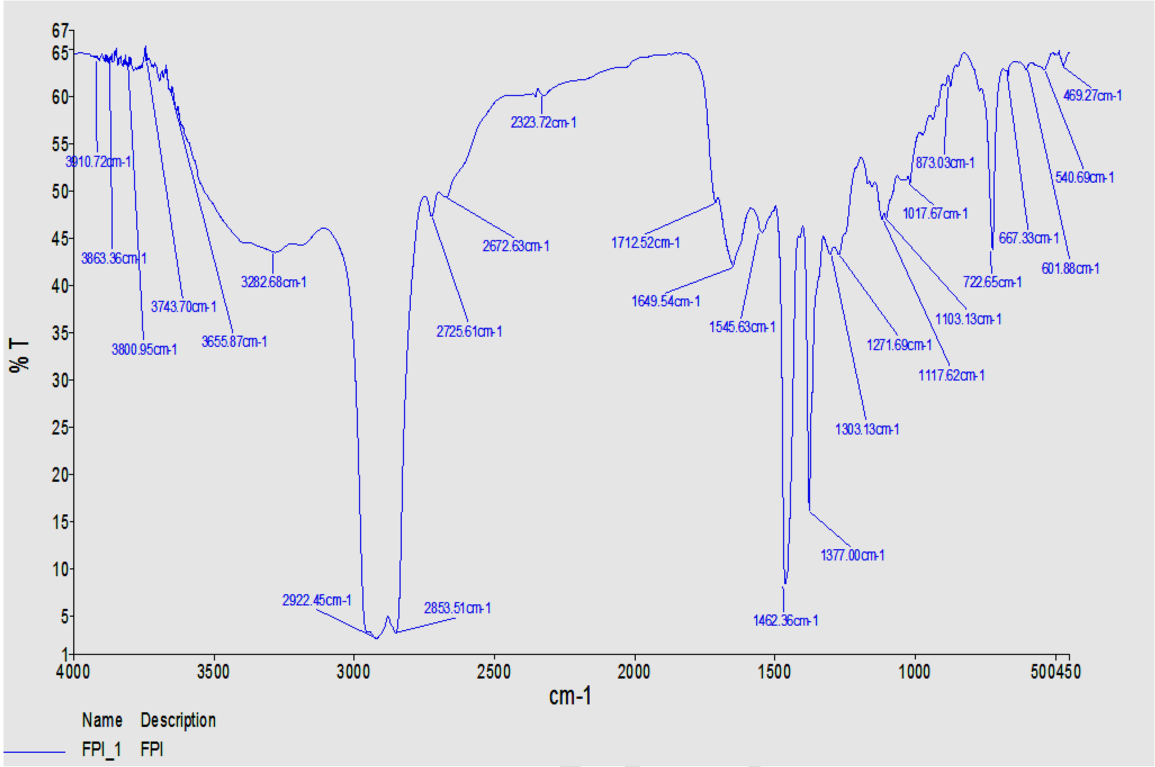

Fig. 1b: FT-IR spectrum of corrosion products of MS in the presence of HCl extract of *Carica papaya* leaves

3.2 Gravimetric measurements

The gravimetric monitoring of corrosion rate (C_R) and inhibitors efficiency (I.E %) is a versatile tool because of the simplicity of the method and this has been employed by several researchers [15-18]. The plot of the variation in mass loss of the mild steel substrates in the absence and presence of varying concentrations CPLE (yellow) as a function of exposure time at 30^{o}C and different extract concentrations is shown in Fig. 2. The C_R and I.E % values obtained from the weight loss experiment at varying concentration of CPLE (yellow) in 1M HCL solution are also shown in Table 1. The results showed that the mass loss increased with increase in exposure time in the blank solution. However, the addition of the inhibitor extracts resulted in a considerable decrease in the mass loss of mild steel substrate in comparison with the blank solution. The reduction is attributed to the adsorption of the extract active constituents (heterocyclic compounds) on the mild steel substrate as revealed by some notable changes in the FT-IR spectral analysis. The adsorption of the extract active constituents as was observed indicates the formation of a protective layer which prevents charge and mass flow between the mild steel and the aggressive solution [3]. This can also be due to the fact that the extract active principles are known to combine with the mild steel corrosion products to form a passive film, thus protecting the material from further attack by the HCl solution [19].

Moreover, the C_R as indicated in Table 1 decreases noticeably with increase in inhibitor concentration, that is, the inhibition efficiency (IE) increases with increase in the concentration inhibitor extract. The progressive increase of the extract shows greater reduction of corrosion rate, given maximum inhibitive efficiency of 94.68% at 0.5g L^{-1} at 30°C. The inhibitive effects of the inhibitor is attributed mainly to the presence of hetero atoms such as O, N, S and carbonyl rings with π bands in their constituents which was in tandem with the FTIR results. Hence, the *Carica papaya* leaves extract (yellow), CPLE (yellow) in this regard, acted as an efficient inhibitor for the corrosion of mild steel in 1 M HCl solution.

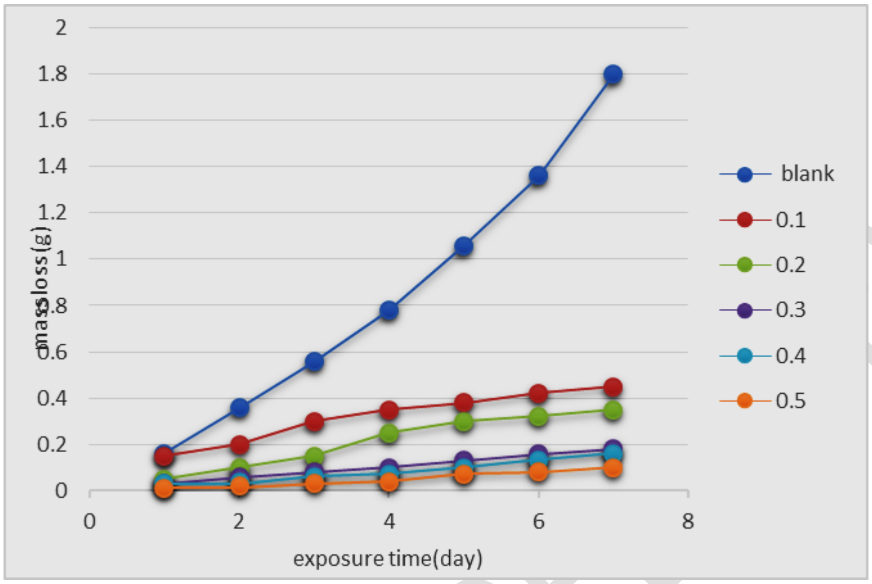

Fig. 2: Mass loss as a function of time for mild steel in 1M HCl in the absence/presence of CPLE (yellow).

3.3 Electrochemical measurements

3.3.1 LPR measurement

The values of the polarization resistance (P_R) obtained from linear polarization studies are listed in Table 1. The values of P_R show a gradual and spontaneous increase with increase in CPLE and reach its maximum at 0.5g L^{-1} concentration (917.3Ω) in comparison to the blank (47.64Ω). Thus, the increase in the polarization resistance in the presence of CPLE (yellow) suggests that a non-conducting adsorbed film is formed at the mild steel acid interface.

3.3.2 Potentiodynamic polarization measurement

Potentiodynamic polarization plots shown in Fig, (3-8) characterizes the behaviour of mild steel with blank solution and varying concentration of CPLE (yellow) at 30°C in 1M HCl acid solution. Electrochemical kinetic parameters associated with polarization measurements such as anodic, and cathodic Tafel constants (β_a and β_c), corrosion potential (E_{corr}), and corrosion current density (i_{corr}) and percentage of inhibition efficiency were obtained and are indicated in Table 1. It is revealed from Figs (3-8) that in the presence of inhibitors both the anodic metallic dissolution and cathodic hydrogen evolution curves shift towards the lower current density. An inspection of the data in Table 1 reveals that as CPLE (yellow) were added, the value of i_{corr} decreases significantly due to the inhibitor molecules which form a blocking barrier on the surface by decreasing the sites of the metal surface of the corrosion causing inactivation. This is purely physisorption phenomenon (adsorption) which involves a retardation of anodic reactions in the process.

Table 1: Corrosion parameters obtained from potentiodynamic polarization and linear polarization data of mild steel in 1M HCl in the presence of different concentrations of CPLE (yellow) at 30^{o}C

Gravimetric measurement (weight loss) 24hrs immersion				Potentiodynamic polarization and linear polarization resistance data							
S/N	Conc.	$C_{R\ mm/yr}$	I.E %	E_{CORR}(v)	I_{CORR}(A)	b_a v/dec	b_c v/dec	$C_{R\ mm/yr}$	I.E%	P_R (Ω)	I.E %
1	Blank	0.1881	-	-0.6816	9.926E -05	0.026181	0.018646	1.1534	-	47.64	-
2	0.1	0.1763	6.27	-0.5658	7.1032E-05	0.017185	0.019318	0.8149	28.4	56.320	15.41
3	0.2	0.0587	68.79	-0.5239	6.4847E-05	0.016166	0.018696	0.7535	34.7	58.061	17.94
4	0.3	0.0530	71.82	-0.5186	1.823E -05	0.018792	0.021694	0.2118	81.6	239.89	80.14
5	0.4	0.0353	81.20	-0.5890	7.7249E-06	0.019819	0.022375	0.0898	92.2	590.72	91.94
6	0.5	0.0100	94.68	-0.9746	3.8824E-06	0.015804	0.017043	0.0451	96.1	917.30	94.80

Also the value of E_{corr} shifts significantly towards more negative direction, with 0.5 g L^{-1} concentration given -0.9246V compared to the blank given a value of -0.6816V. Moreover, the largest displacement in E_{corr} value observed at a concentration of 0.5g L^{-1} is 0.456V (456mV) which is greater than 0.085V (85mV). If the value of E_{corr} shifts beyond 85mV, an inhibitor is designated as an anodic or cathodic type [6, 20]. The Tafel slopes, β_a and β_c, show slight variations in the presence of the extract, suggest that the inhibitive effects take place via a simple blocking of existing anodic and cathodic sites on the metal surface [21]. Hence, the above trend is in tandem with the gravimetric measurements and proposed that CPLE (yellow) acts as an efficient mixed-type inhibitor. A green extract that shows both physisorption and chemisorption phenomena will result in a higher efficiency of inhibition compared to the individual physisorption or chemisorption mechanism [22, 23].

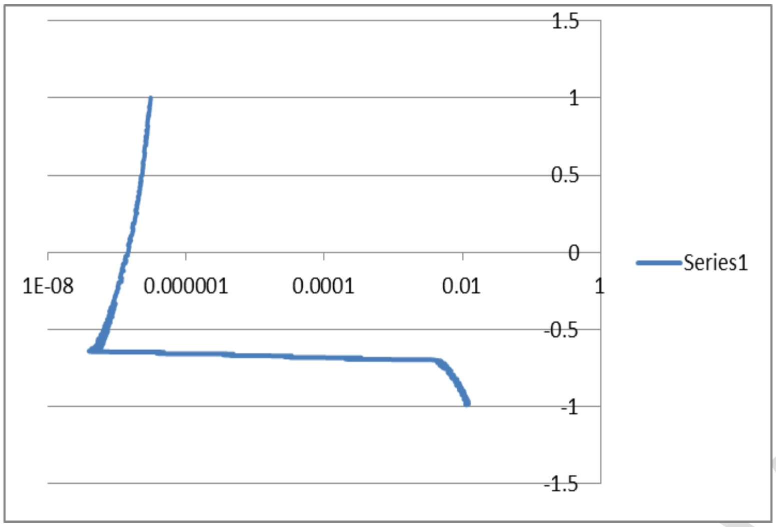

Fig. 3: Tafel plot of MS immersed in 1M HCl without CPLE (yellow)

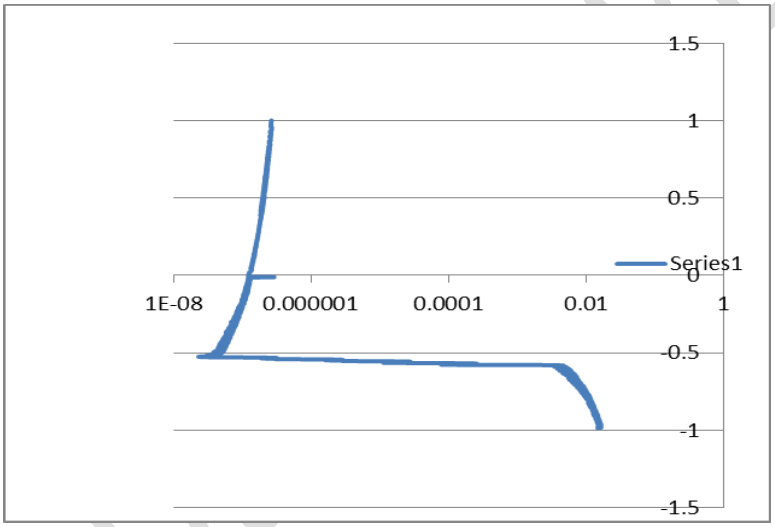

Fig. 4: Tafel plot of MS immersed in 1M HCl with 0.1g L^{-1} CPLE (yellow) at 30^{o}C

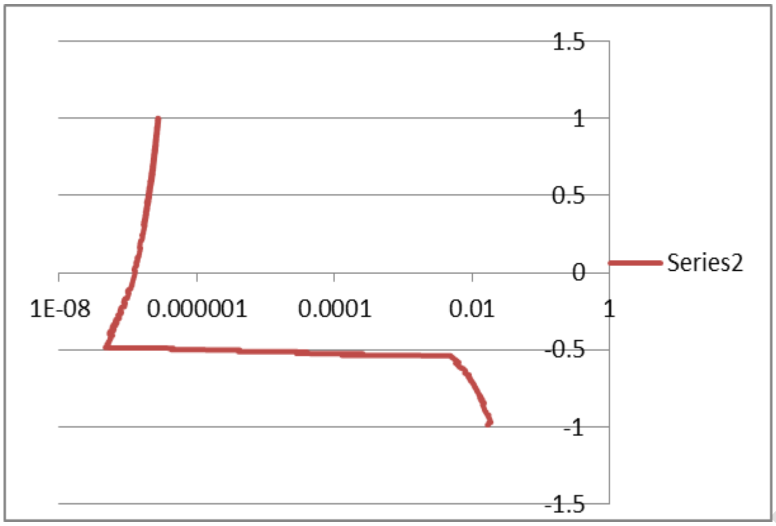

Fig. 5: Tafel plot of MS immersed in 1M HCl with 0.2g L^{-1} CPLE (yellow) at 30^{o}C

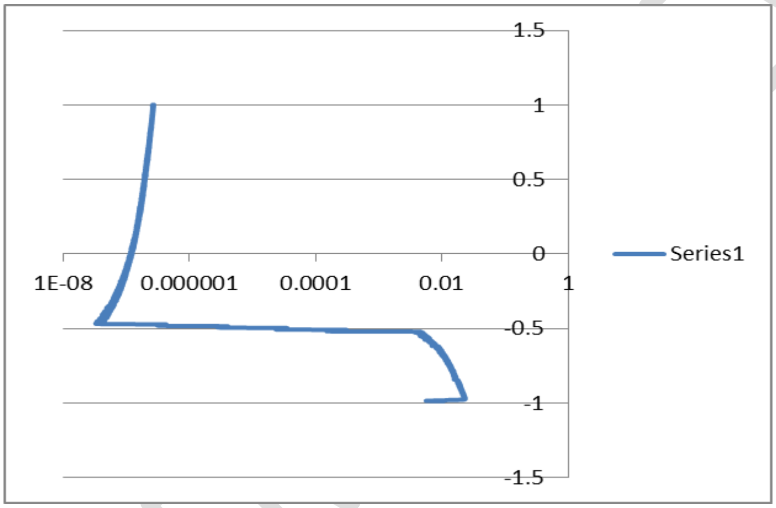

Fig. 6: Tafel plot of MS immersed in 1M HCl with 0.3g L^{-1} CPLE (yellow) at 30^{o}C

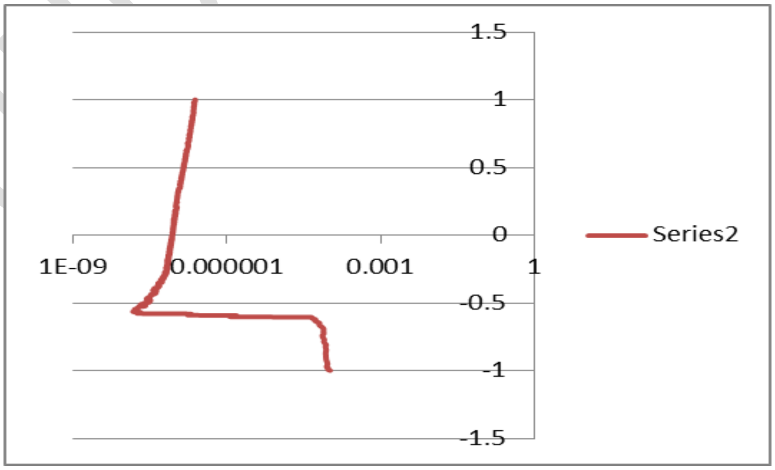

Fig. 7: Tafel plot of MS immersed in 1M HCl with 0.4g L^{-1} CPLE (yellow) at 30^{o}C

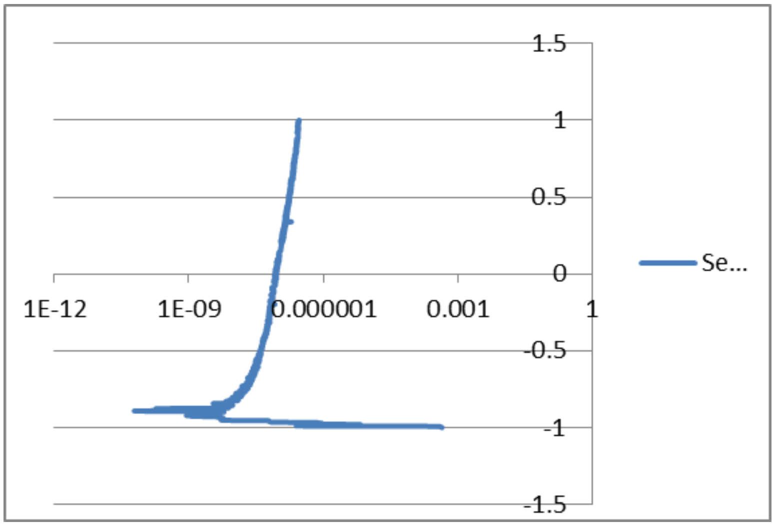

Fig. 8: Tafel plot of MS immersed in 1M HCl with 0.5g L^{-1} CPLE (yellow) at 30^oC

Table 2: Adsorption parameters of ethanolic extract of CPLE (yellow) on the mild steel in 1M HCl at 30˚C using potentiodynamic polarization

Time hr	***Conc.*** ***$C_{inh}(gl^{-1})$***	***Θ***	***log θ***	***θ/C***	***log θ/C***	***log C***	***1-θ***	***log(1-0)***	***(θ/1-θ)***	***log θ/1-θ***
24	Blank	-	-	-	-	-	-	-	-	-
	0.1	0.284	-0.5467	2.840	0.4533	-1.000	0.716	-0.1451	0.3966	-0.4016
	0.2	0.347	-0.4597	1.735	0.2393	-0.699	0.653	-0.1851	0.5314	-0.2746
	0.3	0.816	-0.0883	2.720	0.4346	-0.5229	0.184	-0.7352	4.4348	0.6469
	0.4	0.922	-0.0353	2.305	0.3627	-0.3979	0.078	-1.1079	11.8205	1.0726
	0.5	0.961	-0.0173	1.922	0.2838	-0.3010	0.039	-1.4089	24.6410	1.3917

3.4 Adsorption isotherms

In corrosion studies, further information required elucidating the adsorption mechanism between the inhibitor molecules and the surface of metallic substrate can be obtained from adsorption isotherm. The data were made to fit into Langmuir, Temkin, Freundlich, El-Awady, and Flory – Huggins isotherms, but the R^2 values for each isotherm model were used to verify the most suitable model. From the correlation (R^2=0.9986) obtained, the El-Awady isotherm model was found to be the best that describes the adsorption mechanism of *Carica papaya* extract (yellow) on mild steel in hydrochloric acid solution. Hence, El–Awady adsorption isotherm is appropriate for evaluating the adsorption equilibrium constant, $K_{ads.}$

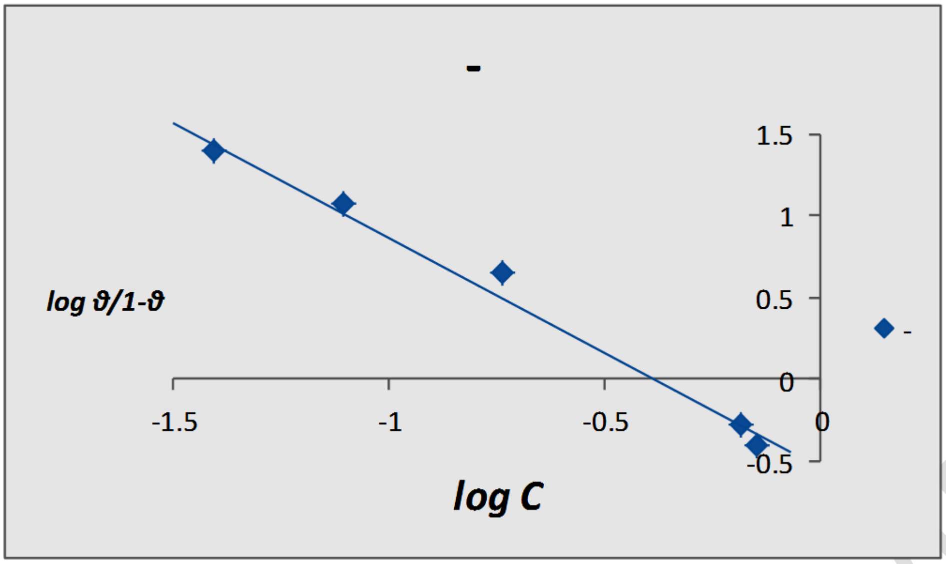

Fig. 9: El- Awady isotherm

3.5 Thermodynamic parameters

Free energy of adsorption (ΔG_{ads}) can be calculated, thus using the equation

$$\Delta G_{ads} = - RT \ln (55.5K_{ads}) \qquad (5)$$

where R is the molar gas constant, T is the temperature and 55.5 is the molar concentration of water in solution. The value K_{ads} calculated from the intercept of the linear graph is related to the standard free energy of adsorption, ΔG_{ads} as shown in equation 5 above. In literature, the values of ΔG_{ads} less than -20KJ/mol signify physical adsorption, which was consistent with electrostatic interaction between charged molecules and a charged metal [24, 25]. The ΔG_{ads} value calculated using the El-Awady isotherm plot was found to be -14.9KJ.mol^{-1}, an indication of physisorption (adsorption) phenomenon. The value of ΔG_{ads} is found to be negative, indicating that the adsorption is spontaneous.

4. Conclusions

Experimental analysis of the corrosion inhibition properties of *Carica papaya* leaves extract (yellow) CPLE (yellow) showed the constituents to be an efficient inhibitor in the acidic medium at 30°C, giving a maximum inhibition efficiency of 94.68% and 96.1% from weight loss and potentiodynamic polarization methods respectively. The significant changes as observed in the FTIR spectral analysis suggested that some adsorption over the mild steel surface had taken place as revealed by a protective layer. Moreover, the adsorption mechanism was found to obey the El-Awady isotherm. Thermodynamic evaluation deduced revealed a physisorption with the mild steel surface and spontaneous adsorption of CPLE (yellow). The environmentally benign inhibitor could as well find possible applications as chemical cleaning in industries.

The field of green corrosion inhibitors is still an open issue, and concerted efforts are continuously evolving considering the huge benefits when the matter of reducing wastes, effect of toxins and perhaps, value addition is debated. However, one of the drawbacks when investigating the corrosion inhibition efficiency of the organic compound is related to the diversity in its chemistry. Does all the organic molecules in plant extract responsible for inhibitive property? Is inhibition a function of the synergy of organic molecules? Are there some components that could weaken the inhibiting ability of others? What is the exact inhibition mechanism by plant extracts? Hence, further works are still needed to further deepen our knowledge on the adsorption mechanism and inhibitor – metal interactions based on theoretical studies within the dynamic functional theory and molecular dynamics frameworks. Based on the results presented, the future direction of the current research will focus on optimizing the inhibitor formulations in order to isolate the required applied corrosion inhibitor concentration while achieving the maximum attainable corrosion inhibition performance. This could be carried out by isolating the organic molecules responsible for the inhibition effect, viz-a-viz other variables, such as concentration of the organic molecules and temperature and, moreover, optimizing the variables statistically.

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