Mitigation of the Corrosion of Mild Steel in Acidic Solutions Using An Aqueous Extract of *Calopogonium muconoide* (cm) as a green corrosion inhibitor

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Abstract: The applications of inorganic and some organic corrosion have received several setbacks because of their toxicity. Consequently, current research interests are directed toward the design, synthesis and application of green corrosion inhibitors. This paper reports the use of the ethanol extract of Calopogonium muconoide against the corrosion of mild steel in 0.5 M hydrochloric acid using weight loss measurements at 303 K and 333 K. Results obtained from weight loss measurements indicated that the plant extract retarded the corrosion of mild steel coupons in the acid media at 91.39 % and 56.79 % inhibition efficiency thereby functioning as a good corrosion inhibitor against the dissolution of steel in 0.5 M hydrochloric acid. The inhibition efficiency of plant extract on mild steel in 0.5 M HCl was investigated. The inhibition performance was tested by weight loss technique. The results obtained from the weight loss method showed that inhibition efficiencies increase with an increase in the concentration of the plant extract molecules and with the highest inhibition efficiency observed at the optimum concentration of 1.2 g/L. At 303 K and 333 K, the inhibitor showed inhibition efficiency of 91.39 % and 56.79 % respectively. Inhibition efficiencies were also found to decrease with an increase in temperature. Apparent activation energy values in the inhibited systems (35.62 kJ/mol. 39.23 kJ/mol/44.47 kJ/mol, 49.49 kJ/mol, 56.64 and 58.10) were found to be greater than that of the free acid solution (12.98 kJ/mol) showing the adsorption of the plant extract on the steel surface to be by physical The following adsorption mechanism. isotherms were implored in the study;

Freundlich, El-Awardy et al and Langmuir isotherms with Langmuir showing the best description of the experimental data with correlation coefficient value ($R^2 > 0.99$). In the study, values of enthalpy, ΔH were all negative showing the exothermic nature of the corrosion and inhibition processes while free energy values for the inhibition processes at 303 and 333 K were -16.84 kJ/mol and -15.56 kJ/mol respectively revealing the inhibition of mild steel in the acid media by the plant extracts to be spontaneous except at 1.0 g/L and 1.2 g/L concentrations at both temperatures.

Keywords: Corrosion, mild steel, acidic medium, inhibition, *Calopogonium muconoide leaf extract*

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1.0 Introduction

As a significant alloy in the universe, mild steel is the substance of choice in oil manufactures

for its ability to work mechanical and low coast (Adewuyi and Göpfert, 2014; Anupama et al., 2017). In several industrial processes such as acid cleaning, acid well acidizing, and acid pickling, rust and contaminated scales were generally removed using acid solutions. (Uhlig, 1985). The use of acids during treatment and cleaning processes will lead to corrosion of the metal surface. therefore, an appropriate corrosion inhibitor is urgently needed. Moreover, hydrochloric acid can be produced as a by-product of the crude oil desalting process and some oil refinery treatments (Mitchell, 1998). Hydrochloric and sulphuric acids are the most widely used mineral acids in the pickling processes of metals (Gale and Totemeier, 2003). Organic compounds containing a heteroatom, such as nitrogen, oxygen, sulfur and phosphorus, or containing double and triple bonds, as well as aromatic rings are considered one of the most important materials recognized in practice and used as anti-corrosion inhibitors. To protect mild steel from the corrosive environment and also to reduce the consumption of acidic solutions that occurs during prolonged operation (Mobin et al., 2017; Al-Taweel et al., 2019). Inhibitors can control the dissolution of metals and alloys by twisting a layer of anti-corrosion on the surface of the metal or alloy to prevent corrosion thus not being exposed to an acidic solution (Mourya et al., 2015). The approach of adsorption inhibitor consists of the inhibitor chemical structure and the nature of the solution acid or base (Banerjee et al., 2012). Consequently, inhibitors must be active, not expensive and eco-friendly (Morad, 2008; Abiola and James, 2010). It is generally known that the spontaneous



dissolution of iron in acid solution produces

 ${\rm Fe}^{2+}$ ions, which corresponds to the anodic reaction, accompanied by discharging of electrons by hydrogen evolution at cathodic sites on the metal surface. Because of the general destructive attack of acid solutions. the use of inhibitors to control the aggressiveness of acid environments was found to have widespread applications in many industries (Lalitha et al., 2005). The feasibility of protection methods depends mainly on the conditions and surrounding environment that materials, particularly metals, experience during service conditions. The use of corrosion inhibitors to minimize corrosion rate in closed service systems is well-established and generally accepted (Garai et al., 2012; Anthony et al., 2004). In literature, several organic compounds have reported as potential been corrosion inhibitors for different metals, but on the other hand, ecological and healthy problems have arisen because of using such synthetic compounds. In recent years, a considerable amount of effort devoted to finding low-cost and efficient corrosion inhibitors from natural resources such as plant extracts that can be used as promising alternative sources for corrosion inhibitors (Weina et al., 2014; El-Etre, 2006; Fouda et al., 2015). Several studies published on the use of some plant extract as corrosion inhibitors pivot their purpose on the nontoxicity, eco-friendly, avoidable cost and accessibility as the major factors behind their choices (Zucchi and Omar, 1985; Fouda et al., 2014; Oguzie, 2007). However, to the knowledge of the current researchers little has been reported on the use of this plant leaf as a corrosion inhibitor. Emembolu and Onyenanu (2020) reported inhibition efficiency as high as 91% for the calopogonium mucunoides leaf extract in the literature as a corrosion inhibitor. The present work provides an investigation on using an aqueous extract, simply prepared from the leaves of Calopogonium muconoide, as a green corrosion inhibitor to control the corrosion behaviour of mild steel in a corrosive environment was studied using weight loss techniques. The plant extract was characterized with FTIR spectroscopy.

2.0 Materials and Methods

2.1 Materials

Steel sheets were purchased from the building materials market, Jos. Analytical balance, desiccator, hand dryer, ethanol, acetone, HCl, SiC paper (#600 and #1200). Analar grade reagents.Mild steel coupons of composition (w %) Fe: 99.14, C: 0.15, Mn: 0.60, P: 0.04, and Si: 0.03;and dimension, 3.0cm x 2.0cm x 0.6 cm were used for the experiments. They were abraded with emery papers of variable grades, starting with a coarse one (#600) and proceeding to the finer grade (#1200). The coupons were degreased in ethanol, dried in acetone and warm air, and stored in moisture-free desiccators before use.

The leafy parts of *Calopogonium muconoide* were collected from the Michael Okpara University of Agriculture, Umudike in Abia State. A voucher specimen of the plant was dried by air for six weeks, then pulverized with a pestle and mortar and kept in a desiccator in the laboratory. Five hundred grams of the air-dried and powdered leave parts of the plant were boiled with deionized water three times at 60 °C for 1 h and allowed to cool before filtration. The aqueous extract was concentrated under a vacuum at 40 °C until all the solvents were completely removed. The dried plant aqueous extract was used for the corrosion inhibition experiments by preparing inhibitor test solutions in the concentrations 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L, 1.0 g/L and 1.2 g/L. This was achieved by transferring 0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.25 g and 0. 30 g of the extract into 250 mL of 0.5 M HCl solution in glass jars (Chahul et al. 2019).

2.2 Weight Loss Determination

The procedure for weight loss determination was as communicated (Abiola *et al.*, 2011). Previously weighed mild steel coupons were immersed in 250 mL open beakers containing 100 mL of 0.5 M HCl solution (blank) and then with the addition of different CM concentrations to the 0.5M HCl solution (3 – 20% v/v) at 303 and 333 K. The weight losses



of the coupons were monitored after 24 h immersion period per coupon progressively for a total of 120 h at 303 K and 333 K. A blank was carried out without inhibitor. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance. Duplicate experiments were conducted at the same time and the average weight losses were taken.

The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using equations 1 and 2 respectively,

$$\% IE = \frac{W_2 - W_1}{W_2} \times \frac{100}{1}$$
(1)

CR (mgcm⁻²h⁻¹) =
$$\frac{w_2 - w_1}{Axt}$$
 (2)

Surface Coverage (θ) = $\frac{W_2 - W_1}{W_2}$ (3)

where w_1 and w_2 are the weight losses for the uninhibited and inhibited systems. CR and the corrosion rate and the surface area of the mild steel

3.0 Results and Discussion

In Figs. 1 and 2, weight loss of mild steel in the acid medium (at 303 and 333 K respectively) can be seen to increase with the period of contact between the metal and the acid medium. However, the pattern of variation at both temperatures reveals a minimal decrease in the weight of the metal as the concentration of the plant extract increases. Corrosion rates at various reference concentrations and at 303 and 333 K were calculated and the values obtained are recorded in Table 1. Also calculated and recorded in the same Table 1 are the inhibition efficiencies of different concentrations of the extract.

The weight loss decreased with an increase in the concentration of the inhibitor but decreased with increasing temperature. Consequently, the inhibition efficiency of the extract increases with an increase in its concentration and decreases as the temperature increase from 303 to 333 K. Therefore, the extract is an adsorption inhibitor for the corrosion of the metal and suppresses the rate at which it corrodes (Eddy *et al.*, 2015). This observation can be attributed to an increase in the concentration of inhibitor molecules adsorbed on the metal surface, which separates the mild steel from the acidic solution resulting in the retardation of the metal dissolution (Keles *et al*, 2015). Recorded corrosion rate and inhibition efficiency indicated changes in inhibition efficiency from 18 to 57% as the concentration of the leaf extract varied from 77 to 91% and 18 to 57% as the extract concentration varied from 0.2 to 1.2 g/L and at 303 and 333 K respectively.

Table 1: Inhibition efficiency (%IE) of *Calopogonium muconoide* on the corrosion of mild steel and associated corrosion rate (CR) and degree of surface coverage (θ)

C (g/L)	303 K			333 K		
	θ	CR (mgcm ⁻² h ⁻¹)	% I.E	θ	CR (mgcm ⁻² h ⁻¹)	% I.E
0.0	-	0.0755	-	-	0.1201	-
0.2	0.7669	0.0176	76.69	0.4763	0.0629	47.63
0.4	0.8039	0.0148	80.39	0.4988	0.0602	49.88
0.6	0.8464	0.0116	84.64	0.5266	0.0569	52.66
0.8	0.8768	0.0093	87.60	0.5454	0.0546	54.54
1.0	0.9086	0.0069	90.86	0.5645	0.0523	56.45
1.2	0.9139	0.0065	91.39	0.5679	0.0519	56.79

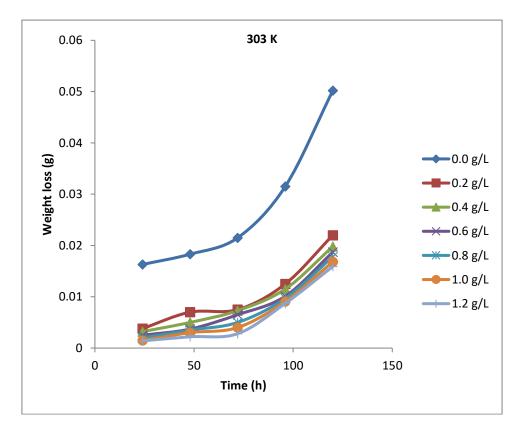


Fig.1: Variation of weight loss (g) of mild steel versus time (h) in the absence and presence of different concentrations of inhibitor at 303 K.



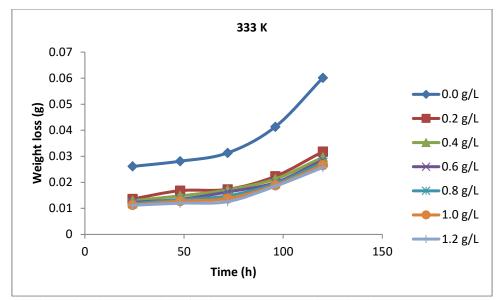


Fig.2: Variation of weight loss (g) of mild steel versus time (h) in the absence and presence of different concentrations of inhibitor at 333 K.

3.2 Kinetics studies

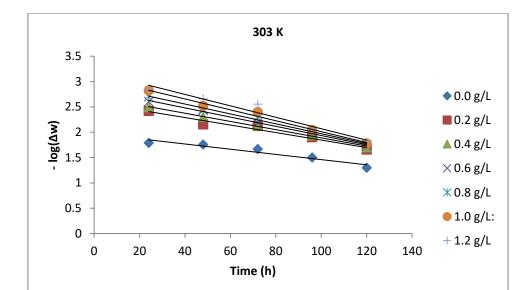
Several literatures have indicated that the corrosion of most metals favours a first order kinetics such that the rate constant and the weight loss has an exponential relationship, that can be expressed as follows (Alamiery, 2021)

$$-\log(\text{weight loss}) = \frac{k_1 t}{2.303}$$
(4)

Equation 7 is a linear model when values of

 $-\log(weight \ loss)$ are plotted against time

(t) as shown in Figs. 3 and 4. Indices deduced from the plots were the rate constant and the half-life of the metals at various concentrations of the inhibitor as shown in Table 2. The good fitness of the data to the kinetic model is affirmed by the excellent values of R^2 and the estimated values half life, $t_{1/2} = 0.693/k_1$) are presented in Table 2. The results show that the inhibitor extended the half life of the metal in 0.5 M HCl. Therefore, CM leaf is an inhibitor for the corrosion of mild steel in HCl (Founda et al., 2014, 2015).



(7)

Fig. 3: Variation of –log weight loss of mild steel with time for the corrosion of mild steel in 0.5 M HCl in the presence of the inhibitor at 303 K.



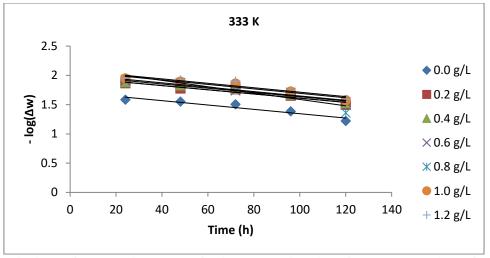


Fig. 4: Variation of –log weight loss of mild steel with time for the corrosion of mild steel in 0.5 M HCl in the presence of the inhibitor at 333 K

The activation energy needed for the corrosion of mild steel (in the absence and presence of CM leaf extract as an inhibitor) was investigated using the Arrhenius equation (equation 4)(Verma *et al.*, 2018). The Arrhenius equation was also applied to evaluate the values of the activation energy (E_a) based on the expression of equation 5 which defines a linear plot of log(CR) versus 1/T (Eddy, 2010)

$$\log(CR) = \ln(A) - \frac{E_a}{2.303RT}$$
 (5)

A plot of log (CR) against $\frac{1}{T}$ for the corrosion of mild steel in the absence and presence of the inhibitor in 0.5 M HCl are shown in Fig. 5. The plot gave a straight line indicating that the Arrhenius equation is obeyed. The calculated values for the thermodynamic parameters are shown in Table 3. The values of the activated energies of the inhibitor on adsorption onto mild steel calculated from the slope and the intercept of the plots are shown in Table 3.

 Table 2: Kinetic parameters for the adsorption of ethanol extract of Calopogonium muconoid on mild steel surface at 303 and 333 K

Temperature	C(g/L)	Slope	R ²	k (h ⁻¹)	t _{1/2} (h)	Intercept
	0.0	-0.051	0.9228	0.11745	5.9004	1.9726
	0.2	-0.0074	0.0592	0.01704	40.6690	2.5853
303 K	0.4	-0.0081	0.9961	0.01865	37.1582	2.6985
	0.6	-0.0091	0.9951	0.02096	33.0630	2.8442
	0.8	-0.0098	0.9917	0.02257	30.7045	2.9461
	1.0	-0.0108	0.9849	0.02487	27.8649	3.0862
	1.2	-0.0113	0.9592	0.02602	26.6333	3.197
	0.0	-0.0037	0.9063	0.00852	81.3380	1.7164
	0.2	-0.0036	0.9276	0.00829	83.5947	1.9687
	0.4	-0.0036	0.9598	0.00829	83.5947	1.9985
333 K	0.6	-0.0037	0.9563	0.00852	81.3380	2.0223
	0.8	-0.0054	0.818	0.01243	55.7522	2.1318
	1.0	-0.0038	0.9236	0.00875	79.2000	2.0736
	1.2	-0.0038	0.8793	0.00875	79.2000	2.0916

The calculated activation energies are in the range expected for the mechanism of physical adsorption since they are less than



the optimum value (80 kJ/mol) expected for a chemical adsorption mechanism (Odoemelam *et al.*, 2009). The results also reveal that the E_a values for the inhibited solutions containing the inhibitor are higher than compared to the activation energy values for the uninhibited solution and this indicates that physisorption may have been the likely mode of adsorption of the inhibitors on the mild steel surfaces (Salman *et al.*, 2018). Also, the activation energy (E_a) of the inhibited solution increases with an increase in the concentration of the inhibitors increase and these also account for the increase in inhibition efficiency as concentration increases. Speaking thermodynamically, the dissolution of mild steel in the presence of the inhibitor is slow for high activation energy leading to a low corrosion rate. This can be attributed to the formation of protective layers on the surface of the metal as the concentration of the inhibitors increases. (Tiwari *et al.*,, 2018).

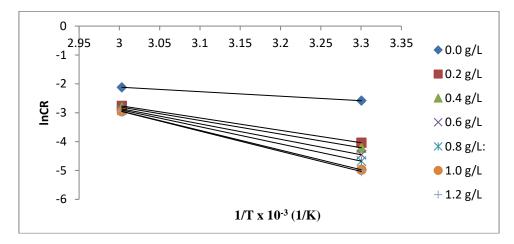


Fig.5: Plots of log CR versus $\frac{1}{T}$ for the corrosion of mild steel in 0.5 M HCl containing various concentrations of inhibitor

. Table 3: Activation parameters for corrosion of mild steel in 0.5 M HCl in absence and
presence of different concentrations of Calopogonium muconoid extract.

C (g/L)	Slope	Intercept	Ea(J/mol)	A(s ⁻¹)	R ² values
0.0	-1.5614	2.5694	12.9815	13.0580	1.0000
0.2	-4.2842	10.099	35.6188	24318.679	1.0000
0.4	-4.7191	11.361	39.2346	85905.231	1.0000
0.6	-5.3491	13.197	44.4724	538746.272	1.0000
0.8	-5.9536	14.971	49.4982	3175577.298	1.0000
1.0	-6.8126	17.508	56.6400	40144660.47	1.0000
1.2	-6.9879	18.026	58.0974	67389515.00	1.0000

3.3 Thermodynamic parameters.

The Transition state equation (equation 7) was used to calculate the enthalpy (ΔH_{ads}) and entropy changes (ΔS_{ads}) for the adoption of the inhibitor on the metal surface (Eddy *et al.*, 2022)

$$log\left(\frac{CR}{T}\right) = log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{ads}}{R}\right) - \left(\frac{\Delta H_{ads}}{RT}\right)$$
(7)

From the slopes and intercepts of the plots of $log\left(\frac{CR}{T}\right)$ versus 1/T (Fig. 6) for various concentrations of the inhibitor, the enthalpy and entropy changes were evaluated (Table 4), The results confirm an exothermic adsorption process with characteristics

increase in the orderliness of the adsorbed species with increasing extract concentration (El-Etre, 2007; (Sigirick *et al.*, 2016)

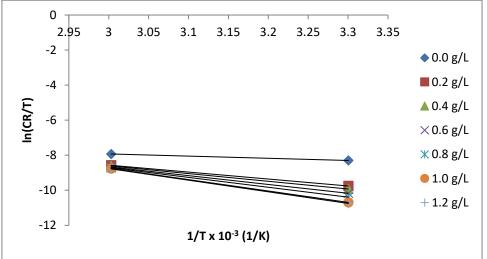


Fig.6: Plot of log $\frac{CR}{T}$ versus $\frac{1}{T}$ for the corrosion of mild steel in 0.5 M HCl containing various concentrations of inhibitor

Conc	Slope	Intercept	ΔH (J/mol)	ΔS (Jmol⁻¹K⁻¹)	R ² values
0.0 g/L	-1.2439	-4.1923	-23.8145	-277.8392	1.0000
0.2 g/L	-3.9664	3.3366	-75.9367	-133.6984	1.0000
0.4 g/L	-4.402	4.6009	84.2763	-109.4934	1.0000
0.6 g/L	-5.0316	6.4353	-96.3300	-74.3738	1.0000
0.8 g/L	-5.6361	8.2092	-107.9031	-40.4125	1.0000
1.0 g/L	-6.4951	10.746	-124.3487	8.1545	1.0000
1.2 g/L	-6.6313	11.136	-126.9563	15.6210	1.0000

Table 4: Entropies and Enthalpies of Activation values for the inhibitor on mild steel

The Gibbs free energy of adsorption (ΔG_{ads}) was calculated using equation 8 with the relation $\Delta G_{ads} = - RTln (55.5K_{ads})$ (8) Table 4 showed that the calculated value of ΔG_{ads} ranged from – 16838 to -15561 kJ/mol. The negative values of ΔG_{ads} indicate that the adsorption of the plant extract on mild steel is a spontaneous process. The negative values also show strong interaction of the inhibitor molecules on the corroding surfaces (Zhang *et al.*, 2016).

The calculated values for ΔG_{ads} were found to be less than -20 kJmol⁻¹, indicating that the process of adsorption of the inhibitor on the surface of the mild steel follow physisorption. The ΔG_{ads} values within -20 kJmol⁻¹ or lower are consistent with electronic interaction between the inhibitor



molecules and the charged mild steel surfaces and this mode of adsorption is known as physisorption.

3.4 Adsorption isotherm

The extent of corrosion inhibition mainly depends on the surface conditions and of the adsorption mode of the inhibitor. Assumptions were made that the uncovered parts of the metal surface are equal to zero and the corrosion process takes place only at these uncovered parts (Mohan and Joseph, 2018). The degree of surface coverage (θ) has been calculated as follows, $\theta = \frac{IE}{100}$ by assuming a direct relationship between surface coverage and inhibition efficiency as presented in Table 5. The efficiency of this compound as a successful corrosion inhibitor mainly depends on its adsorption ability on the metal surface (Laamaria et al., 2016). So, it is essential to know the mode of adsorption and the adsorption isotherm that can give valuable information on the interaction of compounds of inhibitor and metal surface. To better understand the mode of adsorption of the extract on the surface of the stainless steel, the surface coverage values were adjusted in some adsorption isotherms and the values of the correlation coefficient (R^2) were used to determine the best fit.

In this study, the experimental data fitted excellently to the Langmuir adsorption isotherm (Eddy el al., 2014) as shown in Fig. 7. Plotting $\frac{c}{a}$ versus C yielded a straight line with a correlation coefficient (R^2) of 0.9998 and a slope value close to 1. This result showed that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species (Ahamad et al., 2010). This suggests that the adsorption of inhibitor on the metal surface followed the Langmuir adsorption isotherm according to the following equation which is described by

the mathematical form employed of the isotherm: Where C/θ is the ratio of inhibitor concentration to surface coverage, and K is the adsorption equilibrium constant, a correlation between surface coverage (θ) obtained from polarization curves and the concentrations inhibitor of (C).Thermodynamic parameters are important to further understand the adsorption process of inhibitors on steel/solution interface (Table 5). The equilibrium adsorption $\frac{C}{\theta} =$

$$=\frac{1}{K_{ads}} + C \tag{9}$$

In our studies, the negative value calculated of (ΔG_{ads}) ensures the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface (Wang et al., 2012). It is well known that values of (ΔG_{ads}) of -20 kJ.mol⁻¹ and less negative indicate physisorption, while those of order of -40 kJ.mol⁻¹or more negative indicate chemisorption. Thus, the (ΔG_{ads}) value obtained here shows that in the presence of 0.5M HCl, physisorption of plant extract on the stainless steel may occur (Ahamad et al., 2010).

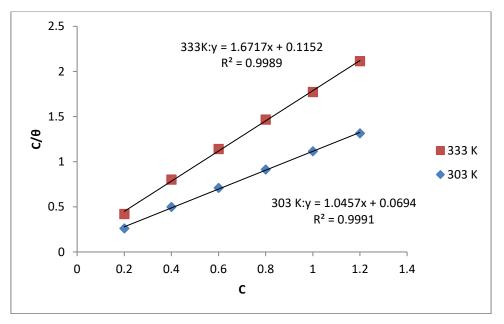


Fig.7: Langmuir adsorption isotherm for the adsorption of inhibitor on the surfaces of mild steel at various concentrations

Table 5: Free Energy and Adsorption Parameters for extract on mild steel

Temperature (K)	Kads	- $\Delta G_{ads}(J/mol)$	R ² values
303	14.4092	16838.5747	0.9991



.5 Scanning Electron Microscopy (SEM) Studies

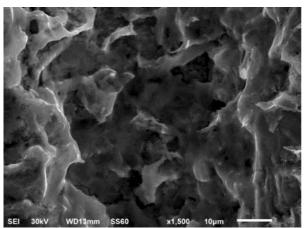
Figure 8 (a and b) represent the micrographs obtained for mild steel samples after being immersed into 0.5 M HCl for 24 h without and with plant extract additive. It is observed that the mild steel surface have suffered from severe dissolution due to exposure to the free acid. There is the formation of corrosion products that presumably covers the entire surface of the material. These corrosion products then form a porous layer that does not allow the protection of stainless steel, hence a severe attack is found. However, the surface of the mild steel is found to be less affected by the aggressiveness of the acid solution when exposed to 0.5 M HCl solution containing 1.2 mg/L of Calopogonium *muconoide* extract. Besides, the morphology of the mild steel surface is smooth compared to the micrograph obtained in case of the mild steel without inhibitor. Moreover, a thin protective layer is formed and evenly distributed on the mild steel surface. This corroborates the involvement of plant extract molecules in blocking the corrosion cells on mild steel surface by decreasing the contact between the mild steel surface and the corrosive solution that sequentially enhances the inhibition characteristics and shows better corrosion protection for the metal surface (Muralidharan et al., 1995; Prabhu et al., 2008).

3.6 FT-IR study

FT-IR spectra *Calopogonium muconoide* leaf extract is shown in Fig. 9. The strong absorption band at 3422 cm⁻¹ is attributed to O-H stretching vibration and that at 2918 cm⁻¹ and 2862 cm⁻¹ relates to C-H stretching vibration. The strong band at1638 cm⁻¹ is assigned to C=O stretching vibration. The C-H bending band in -CH₂ is found to be at 1411 cm⁻¹. Other absorption bands at 1119, 1074 and 1010 cm⁻¹ are due to C-O stretching vibration. The absorption bands below 1000 cm⁻¹ correspond to the aliphatic



C-H group (Li *et al.*, 2012a,b;). This result confirms that the extract contains functional groups such as (O-H) and (C=O).



8(a) Exposed to free acid solution only.

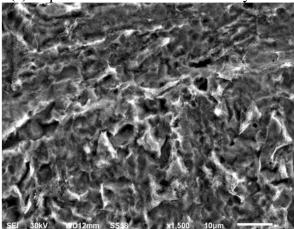


Fig. 8(b) Exposed to test solution containing 1.2 mg/L of *Calopogonium muconoide*

Fig. 8(a and b): SEM images of mild steel surface (a) exposed to free acid solution only and (b) exposed to test solution containing 1.2 mg/L mg/l of *Calopogonium muconoide* extract

4.0 Conclusion

The good accordance between the results obtained from different experimental methods leads to conclude that an aqueous extract of *Calopogonium muconoide* can be used as an effective green corrosion inhibitor for the corrosion of carbon steel in hydrochloric acid solutions. The inhibition efficiency percentages increased with increasing the con- centration of plant extract, but decreased with raising the test solution temperature. The free energy change of adsorption, enthalpy of adsorption and entropy of adsorption indicated that the adsorption process is spontaneous and exothermic and the phytochemical constituents of *Calopogonium muconoide* extract adsorbed at the metal- surface interface and produce a protective barrier by the process of electrostatic adsorption (physisorption). The activation parameters reveal that the activation energy increases as the concentration of *Calopogonium muconoide* increases. Furthermore, the endothermic nature of the mild steel dissolution process can be inferred from the values of activation enthalpy. In addition, the entropy of activation increased with increasing inhibitor concentration; hence, the system disorder is increased.

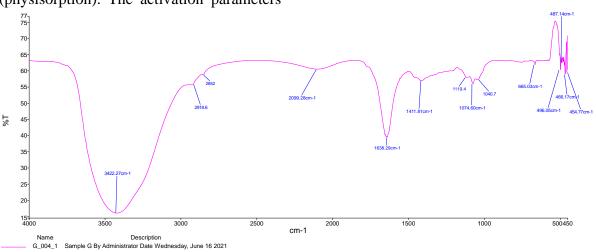


Fig. 9: FT-IR spectral of Calopogonium muconoide leaf extract.

5.0 References

- Abiola , O. K. & James, A. O. (2010). The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution. *Corrosion Science* 52, pp. 661–664.
- Abiola, O. K., Odin, E. M., Olowoyo, D. N. & Adeloye, T. A. (2011). *Gossipiumhirsutum L.* extract as green corrosion inhibitor for aluminium in HCl solution. *Bull. Chem. Soc. Ethiopia*, 25, pp. 475 – 480.
- Adewuyi, A., Göpfert, A. & Wolf, T. (2014). Succinyl amide gemini surfactant from Adenopusbreviforus seed oil: A potential corrosion inhibitor of mild steel in acidic medium. *Ind. Crops Prod.*, 52, pp. 439– 449.
- Ahamad I, Prasad R, & Quraish M. A. (2010). Experimental and theoretical investigations of adsorption of fexofenadine at mild steel/hydrochloric acid interface as corrosion inhibitor.

Journal of Solid State Electrochemistry, 14, 11, pp. 2095-2105.

- Alamiery, A. (2021). Anticorrosion effect of thiosemicarbazide derivative on mild steel in 1 M hydrochloric acid and 0.5 M sulfuric acid: Gravimetrical and theoretical studies, Mater. Sci. Energy Technol. 4, pp. 263–273, <u>https://doi.org/10.1016/</u> j.mset.2021.07.004.
- Al-Taweel, S., Al-Janabi, K., Luaibi, H., Al-Amiery, A. & Gaaz, T. (2019). Evaluation and characterization of the symbiotic effect of benzylidene derivative with titanium dioxide nanoparticles on the inhibition of the chemical corrosion of mild steel. *Int. J. Corros. Scale Inhib.*, 8, pp. 1149–1169.
- Anthony N, Malarvizhi E, & Maheshwari P. (2004) Corrosion inhibition by caffeine-Mn²⁺ system. *Indian. J Chem Technol.* 11(3), pp. 346–350
- Anupama, K. K., Ramya, K. & Joseph, A. (2017). Electrochemical measurements and theoretical calculations on the



inhibitive interaction of Plectranthusamboinicus leaf extract with steel hvdrochloric acid. mild in Measurement, 95, pp. 297-305.

- Banerjee, S.; Srivastava, V., & Singh, M.M. (2012). Chemically modifed natural polysaccharide corrosion as green inhibitor for mild steel in acidic medium. Corros. Sci., 59, pp. 35-41.
- Chahul, H. F., Orhemba, D.T. & Gbadamosi, T.A. (2019): Influence of Cissus populnea Stem Extract on Kinetics and Thermodynamics of Mild Steel Corrosion in Acidic Medium. Ovidius University Annals of Chemistry, 30(1), pp. 14 - 20.
- Eddy, N. O. (2010). Adsorption and inhibitive properties of ethanol extract of Garcinia kola and Cola nitida for the corrosion of mild steel in H₂SO₄. Pigment and Resin Technology, 39, 6, pp. 347-353.
- Eddy, N. O., Ameh, P. O., Emaikwu, V. & Odiongenyi, A. O. (2014). Chemical Information from GCMS and FTIR studies on Ficusthonningii Gum and its Potential as a Corrosion Inhibitor for Aluminuim Acidic Medium. in International Journal Chemical, of Material and Environmental Research. *1*(1), pp. 3-15.
- Eddy, N. O., Momoh-Yahaya, H. & Oguzie, E. E. (2015). Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCL. Journal of Advanced Research. 6, 2, pp. 203-217.
- Eddy, N. O., Odoemelam, S. A., Ogoko, E. C., Ukpe, R. A., Garg, R. & Anand, B. (2022). Experimental and quantum chemical studies of synergistic enhancement of the corrosion inhibition efficiency of ethanol extract of Carica papaya peel for aluminum in solution of HCl. Results in Chemistry, 100290, https://doi.org/10.1016/j.rechem.

2022.100290.

- El-Etre, A. Y. (2006) Khillah extract as inhibitor for acid corrosion of SX 316 steel. Appl Surf Sci, 252(24), pp. 8521-8525
- El-Etre, A. Y. (2007). Inhibition of acid Li, L., Zhang, X., Lei, J., He, J., Zhang, S. & corrosion of carbon steel usingaqueous

extract of olive leaves. J Colloid Interface Sci, 314 (2), pp. 578–83.

- Emembolu, L. N. & Onvenanu, C. N. (2020). Statistical evaluation of calopogonium mucunoides leaf extract as natural inhibitor for mild steel in alkaline media. International Journal of Advanced Research in Science, Engineering and Technology, 7 (7) pp.14313-14319.
- Fouda, A. S., El-Awady, G. Y. & Abousalem, A. S. (2014). Corrosion inhibition and thermodynamic activation parameters of arcatium lappa extract on mild steel in acidic medium. Chem Sci Rev Lett, 3(12), pp. 1277–1290
- Fouda, A. S., Nofal, A. M., El-Ewady, G. Y., & Abousalem, A. S. (2015). Eco- friendly impact of rosmarinus officinalis as corrosion inhibitor for carbon steel in hydrochloric acid solutions. Der Pharma Chemica, 7(5), pp. 183–197
- Gale, W. F., & Totemeier, T. C. (Eds.) (2003) Smithells metals reference book. Butterworth-Heinemann, UK
- Garai, S., Jaisankar, P., Singh, J. K., & Elango, A. (2012). A comprehensivestudy on crude methanolic extract of artemisia pallens(Asteraceae) and its active component effective as corrosioninhibitors of mild steel in acid solution. Corros Sci, 60 pp. 193 204
- Keles, H., Emir, D. M. & Keles, M. (2015). A comparative study of the corrosion inhibition of low carbon steel in HCl solution by an imine compound and its cobalt complex. Corros. Sci., 101, pp. 19-31.
- Laamaria, M. R., Benzakour, J., Berrekhis, F., Derjaa, A., & Villemin, D. (2016). Adsorption and corrosion inhibition of carbon steel inhydrochloric acid medium by hexamethylenediaminetetra(methylene phosphonic acid). Arab J. Chem, 9(1), pp. 245-251,
- Lalitha, A., Ramesh, S., & Rajeswari, S. (2005). Surface protection of copper in acid medium by azoles and surfactants. Electrochim Acta, 51(1), pp. 47–55
- Pan, F. (2012a). Adsorption and corrosion



inhibition of Osmanthus Fragran leaves extract on carbon steel. *Corros.* Sci. 63, pp. 82–90.

- Li, X., Deng, S., & Fu, H. (2012b). Inhibition of the corrosion of steel in HCl, H₂SO₄ solution by Bamboo leaf extract. *Corros Sci.*, 62, pp. 163–175.
- Mitchell, K. E. (1998) US Patent 5,746,908. U.S. Patent and Trademark Office, Washington
- Mobin, M., Aslam, R., Zehra, S. & Ahmad, M. (2017). Bio-/Environment-Friendly Cationic Gemini Surfactant as Novel Corrosion Inhibitor for Mild Steel in 1M HCl Solution. J. Surf. Deterg. 20, 57–74.
- Mohan, R, & Joseph, A. (2018). Corrosion protection of mild steel inhydrochloric acid up to 313 K using propyl benzimidazole:electroanalytical, adsorption and quantum chemical studies.*Egypt J Pet.*, 27(1), pp. 11–20.
- Morad, M. S. (2008). Inhibition of iron corrosion in acid solutions by Cefatrexyl: Behaviour near and at the corrosion potential. *Corros. Sci.* 50, pp. 436–448.
- Mourya, P., Singh, P., Tewari, A. K., Rastogi, R. B. & Singh, M. M. (2015). Relationship between structure and inhibition behavior of quinolinium salts for mild steel corrosion: Experimental and theoretical approach. *Corros. Sci.*, 95, pp. 71–87.
- Muralidharan, S, Phani, K. L. N. & Pitchumani, S. (1995). Polyaminobenzoquinone polymers: a new class of corrosion inhibitors for mild steel. J. *Electrochem Soc.*, 142(5), pp. 1478–1483
- Negri, G., Santi, D. & Tabach, R. (2013). Flavonol glycosides found in hydroethanolic extracts from Tilia cordata, a species utilized as anxiolytics. Revista Brasileira de Plantas *Medicinais*, 15(2), pp. 217–224
- Odoemelam, S. A., Ogoko, E. C., Ita, B. I. & Eddy, N. O. (2009). Inhibition of the corrosion of zinc in H₂SO₄ By 9-deoxy-9a-aza9a-methyl-9a-homoerythromycin A (azithromycin). *Portugaliae Electrochimica acta*, 27, 1, pp. 57-68
- Oguzie, E. E. (2007) Corrosion inhibition of aluminium in acidic and alkaline media

by Sansevieria trifasciata extract. *Corros Sci.*, 49, pp. 1527–1539

- Prabhu, R. A., Venkatesha, T. V., & Shanbhag, A. V. (2008) Inhibition effects of some Schiff's bases on the corrosion of mild steel in hydrochloric acid solution. *Corros Sci.*, 50(12), pp. 3356–3362
- Salman, T. A., Al-Azawi, K. F., Mohammed, I. M., Al-Baghdadi, S. B., Al-Amiery, A.
 A., Gaaze, T. S. & Kadhum, A. H. (2018). Experimental studies on inhibition of mild steel corrosion by novel synthesized inhibitor complemented with quantum chemical calculations. *Results Phys.* 10, pp. 291–296.
- Salman, T., Al-Amiery, A., Shaker, L., Kadhum, A. & Takriff, S. (2019). A study on the inhibition of mild steel corrosion in hydrochloric acid environment by 4methyl-2-(pyridin-3-yl)thiazole-5carbohydrazide. *Int. J. Corros. Scale Inhib*, 8, pp. 1035–1059.
- Sigircik, G., Tüken, T., & Erbil, M. (2016). Assessment of the inhibition efficiency of 3,4-diaminobenzonitrile against the corrosion of steel. *Corros. Sci.*, *102*, pp. 437–445.
- Tiwari M, Gupta V K, Singh RA, Ji G, Prakash R. (2018).Donor–acceptor-type configured, dimethylamino-based organic push–pull chromophores for effective reduction of mild steel corrosion loss in 1 M HCl. *ACS Omega*, 3(4), pp. 4081–93,
- Uhlig, H.H.; Revie, R.W. (1985).*Corrosion* and Corrosion Control; Wiley: New York, NY, USA.
- Verma, C., Verma, D. K., Ebenso, E. E., & Quraishi, M. A. (2018). Sulfur and phosphorus heteroatom-containing compounds as corrosion inhibitors: an overview, Heteroatom Chem. 29 (4), pp. e21437,

https://doi.org/10.1002/hc.2018.29.issue-410.1002/hc.21437.

- Wang, L., Zhu, M. J., Yang, F. C, & Gao, C. W. (2012). Study of a triazolederivative as corrosion inhibitor for mild steel in phosphoricacid solution. *Int J. Corros Scale Inhib*, 1–6,
- Weina, S., Tian, Y., & Peng, S. (2014) The influence of sodium hypochlorite biocide



on the corrosion of carbon steel in reclaimed water used as circulating cooling water.. *Appl Surf Sci.*, 315(1), pp. 95–103

- Zhang, D., Tang, Y., Qi, S., Dong, D., Cang, H., & Lu, G. (2016). Te inhibition performance of long chain alkylsubstituted benzimidazole derivatives for corrosion of mild steel in HCl. *Corros. Sci.*, 102, pp. 517–522.
- Zucchi, F, & Omar, I. H. (1985) Plant extracts as corrosion inhibitors of mild steel in HCl solutions. *Surf Tech*, 24(4), pp. 391–399.

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