Original Research Article

GRAVIMETRIC AND ELECTROCHEMICAL ASSESSMENTS OF THE CORROSION INHIBITION POTENTIAL OF *Cola nitida* SEED EXTRACT ON MILD STEEL SURFACE IN HCl SOLUTION

ABSTRACT

Mild steel corrosion inhibition in 1 M HCl solution by semi-pure seed extracts of *Cola nitida* was investigated using gravimetric and electrochemical (potentiodynamic polarization) methods.The results obtained reveal that dichloromethane (DCM) semi-pure seed extracts of *C. nitida* coded Mb4 and Mb5) inhibited mild steel corrosion in hydrochloric acid solution.The inhibition efficiency, by the gravimetric method, increased with increase in the extracts concentration but decreased with increase in temperature. The inhibition efficiency by the potentiodynamic polarization also increased with increase in extract concentration. The evaluated thermodynamic parameters revealed that the corrosion inhibition process was spontaneous and endothermic in nature. Potentiodynamic polarization measurements revealed that the extracts were mixed – type inhibitors sinceE_{corr} values were less than the threshold value of 85 mV.The adsorption of the extracts onto mild steel surface fitted the Temkin adsorption isotherm. Scanning electron micrographs revealed the formation of protective dense film on the steel surface in the presence of the extracts compared to the blank. Physical adsorption has been proposed for the adsorption of *C. nitida*seed extracts onto mild steel surface.

Keywords: *Cola nitida*, Corrosion, mild steel, Temkin isotherm, acidic medium, gravimetric assessment, potentiodynamic polarization

1 INTRODUCTION

Development and industrial revolutions have expanded the use of steel in the construction and fabrication of metallic components. Continuous exposure of metallic structures to aqueous solutions predisposes metals to a degradation process called corrosion [1]. Efforts have been geared by scientists towards professing solutions to the ravaging impacts of corrosion. The use of synthesized organic compounds with heteroatom such as nitrogen, oxygen, sulphur and/or phosphorus as inhibitors has become prominent [2]. However, some of the organic compounds are toxic and environmentally unfriendly. A number of researcheshave been conducted on the extracts of plant materials as potential mild steel corrosion inhibitors in acidic media, such as *Microdesmispuberula* leaf extract[3];*Telfairiaoccindentalis* rind extract[4]; Cashew waste [5];*Jatropha* stem [6]*Pentaclethramacrophylla Bentham* roots [7];*Cumimum cyminum* extract [8]; Papaya Leaves [9] and *Starchytarpheta indica* leaf extract[10]. The need for the formulation of efficient inhibitors to combat the corrosion of metals cannot be over-stressed.

Cola is a genus of about 125 species of trees indigenous to the tropical rain-forest African region [11]. It is classified in the family of Sterculiaceae. The genus of cola contained five species of edible nuts –*C. nitida*, *C. acuminata*, *C. ballayi*, *C.verticillata* and *C.sphaerocarpa*. The latter three species are not known to be cultivated [12]. The mature fruit of Cola species is known as kola nut [13]. It has a bitter flavor and high caffeine content [14; 15]. However, the research focused on the extracts of *C. nitida*which is referenced to have components that possess substantialπ –electron systems and as well as contain heteroatom such as N, O and heterocyclic rings in their structures that could serve as active points for interaction with the metal surface [12]. These characteristics enhance the potentials of the phytochemicals in the extracts to inhibit corrosion of metal. It is on this premise that this research is poised to investigate thecorrosion inhibitory potentials of eco-friendly and less toxic semi-purified isolates from the seed of *C. nitida.*

2 EXPERIMENTAL

2.1 PLANT MATERIAL AND EXTRACTION

Fresh and maturepods containing seeds of *C. nitida* were collected from a plantation in Nsebe, a rural settlement in Obot Akara Local Government Area of Akwa Ibom State and identified by Mrs. E. G. Udoma, a taxonomist in charge of the herbarium in the Department of Pharmacognosy and Natural medicine, Faculty of Pharmacy, University of Uyo with the Voucher No. of UUPH 46.The pods were cut open with a knife and the seeds were removed and washed in water, chopped into pieces, crushed and dried at room temperature ($30 \pm 2^{o}C$) for 24hours. It was then subjected to comparative extraction in which ethanol, acetone, methanol, ethyl acetate and dichloromethane (DCM) were engaged to macerate 500 g per solvent (2.5 L) in glass extraction jars for 72 hours and re-macerated for another 72 hours for maximum yield. The filtrates obtained were concentrated using Grant GLS400 water-bath and a preliminary weight loss analysis was conducted on the extracts and DCM extract was confirmed as the most active fraction. This was weighed (85 g) and preserved in a refrigerator.

2.2 PURIFICATION OF DCM EXTRACT

DCM extract was subjectedto vacuum liquid chromatography (VLC) in order to break down and separate the inherent components into more purified fractions using the following solvent systems: 30 % hexane +70 % DCM; 100 % DCM; 70% DCM +30 % ethyl acetate, 50 % DCM + 50 % ethyl acetate; 30 % DCM + 70 % ethyl acetate and 100 % ethyl acetate. The fractions obtained were pooled based on the similarity of thin layer chromatographic (TLC)plate spectra, thus:V_1 = 100% hexane + 70% hexane + 30% DCM (11.6 g); V_2 = 50% hexane:50% DCM 13.3 g); V_3 = 50% hexane:50% DCM + 30% hexane + 70% DCM (23.8 g) and V_4 = 100%DCM+ 70% DCM + 30% ethyl acetate (10.2 g). Corrosion inhibition of the fractions was tested by weight lossmethod and the percentage inhibition efficiencies (IE %) were in the following order: V_3 (82%) > V_1 (80%) > V_4 (79%) > V_2 (75%).

V_3 (23.8 g) was subjected to silica gel column chromatography (Merck, 60-120 mesh) and gradient-eluted with n-hexane containing increasing quantity of dichloromethane, followed by increasing quantity of ethyl acetate and methanol. Eluates (20 mL each) were collected, monitored on silica TLC plates (Merck, Germany) in DCM (100%) using p-anisaldehyde-sulphuric acid as spray reagent. Seventy fractions were obtained and bulked together based on their similar TLC characteristics (R_f values, color and reaction with spray reagents) to give four semi-pure residues coded A1 – A4. Fractions A1, A2 and A4 were discardedbecause of the quantity obtained was small. Fraction A3, which was gotten in large quantity, was further purified on silica gel by column chromatography using n-hexane in increasing polarity with DCM (1:3, 1: 10 and 3: 7) while purity was monitored with TLC using DCM and hexane (3:1 and 4:1) and this produced two semi-pure compounds coded Mb4 and Mb5.

2.3 MILD STEEL COUPONS

The mild steel sheet used was obtained from Ken-Johnson Nigeria Limited, Uyo, Akwa Ibom State. The steel which had the chemical composition (w/w%): C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09) and Fe (98.83). It was mechanically press - cut into 3.0 x 2.0 x 0.05 cm coupons. A small hole was drilled out at the center of each coupon. The coupons were abraded with P60X, 220 and 450 emery papers to obtain smooth finished surfaces. The coupons were rinsed with deionized water to get rid of organic impurities, washed in ethanol to remove grease and thereafter in acetone to remove oil. The cleaned coupons were preserved over calcium chloride in desiccators prior to use.

The dimension of the coupons for electrochemical experiment was 1.0 cm x 1.0 cm. They were also polished to a smooth finish.

2.4 GRAVIMETRIC ASSESSMENTS

Gravimetric tests were carried out under total immersion conditions of the coupons using glass rod and hook in 100 ml of 1M HCl solution containing *C. nitida*extract (inhibitor) and blank, respectively, in a beaker maintained at 303 K. One coupon was placed in each beaker. Mild steel coupons were retrieved from the inhibited and blank solutions at intervals of two hours, immersed in 20% NaOH solution containing 200 gL^{-1} of zinc dust, scrubbed with bristle brush, washed in distilled water, dried in acetone and reweighed [16] to determine weight loss with respect to time. This was done for five consecutive times giving a total of ten hours per temperature. The weight loss was taken to be the difference between the initial weight and the weight of the coupons at a given time for the chosen temperature range. The procedure was repeated at 313 K, 323 K and 333 K. From the data, corrosion rate (CR), surface coverage (θ) and percentage inhibition efficiency (IE%) were determined using the following equations [17]:

$$\mathrm{CR} = \frac{\mathrm{W_1 - W_2}}{\mathrm{St}} \qquad (1)$$

where $W_1$is the mass of mild steel coupon before immersion, $W_2$is the mass of mild steelcoupon after immersion, S is the total surface area of the coupon and t is the corrosion time in hours.

$$\theta = \frac{CR_o - CR}{CR_o} \tag{2}$$

$$IE\ \% = \theta x\ 100 \tag{3}$$

where CR_o and CR are corrosion rates of the mild steel coupon in 1.0 M HCl in the absence and presence of the extracts, respectively.

2.5 POTENTIODYNAMIC POLARIZATION MEASUREMENTS

The polarization curve was recorded under potentiodynamic polarization at conditions of air atmosphere and it was controlled by a personal computer. After the open circuit potential had been established (1800s), potentiodynamic polarization curves were obtained at a scan rate of 1mV s^{-1} in the potential range from -0.25 V to 0.25 V. Application of a small potential drop (ΔE) generates a corresponding current flow (Δl) [18].

The corrosion rate of the system was determined using corrosion current density, i_{corr} . The linear portions of the anodic and cathodic Tafel curves were extrapolated to the corrosion potential (E_{corr}) and the corrosion current (i_{corr}) axes. All potentials were measured against Saturated Calomel Electrode (SCE). The surface coverage (θ) and the percentage inhibition efficiency (% IE), were evaluated using equations. (2) and (3) [19]:

$$\theta = \frac{i^o_{corr} - i_{corr}}{i_{corr}} \tag{4}$$

$$IE\% \ = \theta x\ 100 \tag{5}$$

values of corrosion current density in the absence and presence of inhibitor are given by i^o_{corr} and i_{corr} , respectively [20;21].

2.6 SCANNING ELECTRON MICROSCOPY (SEM)

Mild steel coupons were ground with SiC paper having 1000 grit, washed in distilled water and then in ethanol, dried in compressed air and then placed in a fume hood. Morphological survey was conducted on 1 cm x 1 cm area of the surface of mild steel coupons before and after immersion in both blank and test solutions. Thermo Fisher Scientific Prisma E scanning electron microscopy was used.

3 RESULTS AND DISCUSSION

3.1 GRAVIMETRIC MEASUREMENTS

3.1.1 EFFECT OF EXTRACT CONCENTRATION ON INHIBITION EFFICIENCY

Figures 1 and 2 give variation of the inhibition efficiency with the concentration of the semi-pure extracts of *C. nitida* (Mb4 and Mb5) in 1M HCl solution. It is observed that the highest inhibition efficiency obtained was 80.83 % (Mb4) and 69.17 % (Mb5) at 5.0 x 10^{-4} g/L of the extract concentration at 303 K. An increase in the inhibition efficiency with increase in the extract concentration is a pointer to a strong interaction between the extract and the steel surface [22].Comparatively, it is observed that Mb4 inhibited mild steel better than Mb5 (Tables 1 and 2).

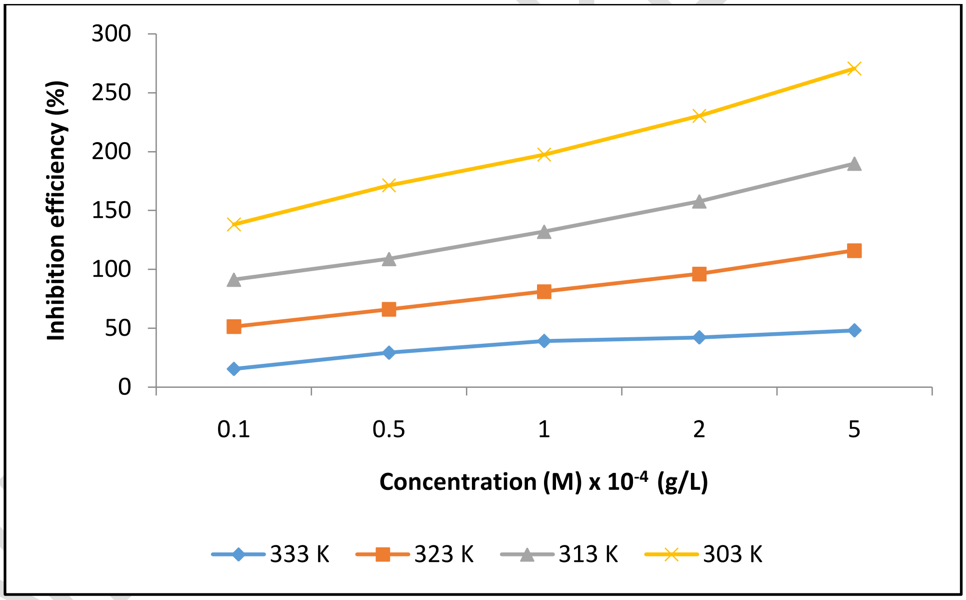


Figure 1: Effect of semi-pure extract of *C. nitida* (Mb4) on the corrosion inhibition efficiency of mild steel at different temperatures.

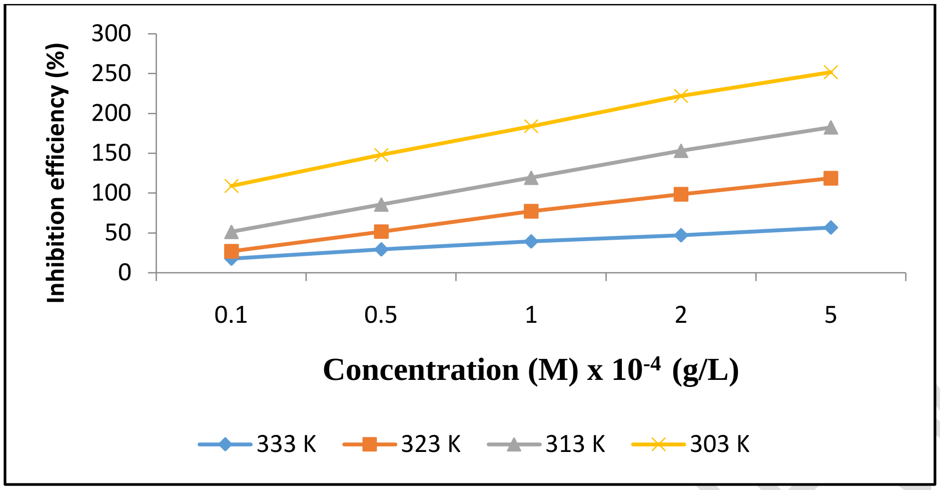


Figure 2: Effect of semi-pure extract of *C. nitida* (Mb5) on the corrosion inhibition efficiency of mild steel at different temperatures.

Table 1:Calculated values of weight loss, corrosion rate andinhibition efficiencyfor mild steelcorrosion in 1 M HCl in the absence and presence of different concentrations Mb4.

Extract Conc. (x 10^{-4})	Weight loss (g)				Corrosion rate (mg cm^{-2} hr^{-1})				Inhibition efficiency (%)			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	0.150	0.248	0.317	0.421	2.40	3.97	5.07	6.74	-	-	-	-
0.1 g/L	0.080	0.149	0.205	0.357	1.28	2.38	3.28	5.71	46.77	40.05	35.31	15.28
0.5 g/L	0.056	0.142	0.200	0.299	0.90	2.27	3.20	4.78	62.50	42.82	36.88	29.08
1.0 g/L	0.052	0.122	0.184	0.257	0.83	1.95	2.94	4.11	65.42	50.88	42.01	39.02
2.0 g/L	0.041	0.095	0.146	0.244	0.66	1.52	2.34	3.90	72.50	61.71	53.85	42.14
5.0 g/L	0.029	0.065	0.102	0.219	0.46	1.04	1.63	3.50	80.83	73.80	67.85	48.07

Table 2:Calculated values of weight loss, corrosion rate and inhibition efficiency for mild steelcorrosion in 1 M HCl in the absence and presence of different concentrations Mb5.

Extract Conc. (x 10^{-4})	Weight loss (g)				Corrosion rate (mg cm^{-2} hr^{-1})				Inhibition efficiency (%)			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	0.150	0.248	0.317	0.421	2.40	3.97	5.07	6.74	-	-	-	-
0.1 g/L	0.064	0.167	0.288	0.280	1.02	3.00	4.61	5.55	57.50	24.43	9.10	17.66
0.5 g/L	0.057	0.134	0.246	0.239	0.91	2.62	3.94	4.77	62.08	34.00	22.29	29.23
1.0 g/L	0.053	0.114	0.197	0.198	0.85	2.30	3.15	4.10	64.58	42.07	37.87	39.17
2.0 g/L	0.049	0.093	0.153	0.173	0.78	1.81	2.45	3.58	68.75	54.41	51.68	46.88
5.0 g/L	0.046	0.080	0.120	0.150	0.74	1.44	1.92	2.93	69.17	63.73	62.13	56.53

The weight loss values decreased with increase in the extract concentration. The data indicate that more of the Mb4 and Mb5 molecules were needed to largely cover a wider steel surface area, thereby arresting attack by aggressive ions and thus, inhibit corrosion [23].

The corrosion behavior of mild steel in a corrodent is captured by the extent it dissolves and this is a reflection of the corrosion rate. Therefore, CR is one of the prime parameters in corrosion studies [24]. Corrosion rates ofmild steel immersed in 1.0 M solution of HCl in the absence and presence of Mb4 and Mb5 at different temperatures were evaluated using equation (1) and presented in Tables 1 and 2, respectively. The variation of CR with time (Tables 1 and 2) is seen to decrease with increase in the concentration of Mb4 and Mb5. This is attributed to the reduction in the concentration of the corrosive ions from the acidic medium as the corrosion reaction progressed [25].

3.2 ADSORPTION CONSIDERATION

It is important to experimentally evaluate the best fit adsorption isotherm to the surface coverage data in order to assess the interactions between the extractsand the mild steel surface. The best fit was obtained with Temkin adsorption isotherm given as [26]:

$$e^{f\theta} = K_{ads}\,C \tag{6}$$

where $\theta$is the surface coverage, K_{ads} is the equilibrium constant of adsorption process, C is the inhibitor concentration and f is the factor of energetic inhomogeneity describing the molecular interactions in the adsorption layer (f = -2a)[27].

K_{ads} is related to standard free energy of adsorption, ΔG_{ads}, through the equation [28]:

$$\log K_{ads} = 1.744 - \frac{\Delta G^{o}_{ads}}{2.303\,RT} \tag{7}$$

Linear plots of surface coverage (θ) versus logarithm of inhibitor concentration (*log C*)with correlation coefficients (R^2) within the range $0.902 \leq R^2 \leq 0.997$obtained for Mb4 (Figure 3) and Mb5 (Figure 4) indicate that the extracts obeyed the Temkin adsorption isotherm.The values of K_{ads} connote the strength of adsorption between adsorbate and adsorbent. Large values of K_{ads} reflect efficient adsorption and hence better inhibition efficiency [29]. It is apparent from Table 3 that the values of K_{ads} for both Mb4 and Mb5 are very low and this implies weak interaction (physisorption) between the extracts (Mb4 and Mb5) and the mild steel surface. The negative values of 'a' imply that attraction exists in the adsorption layer [26].

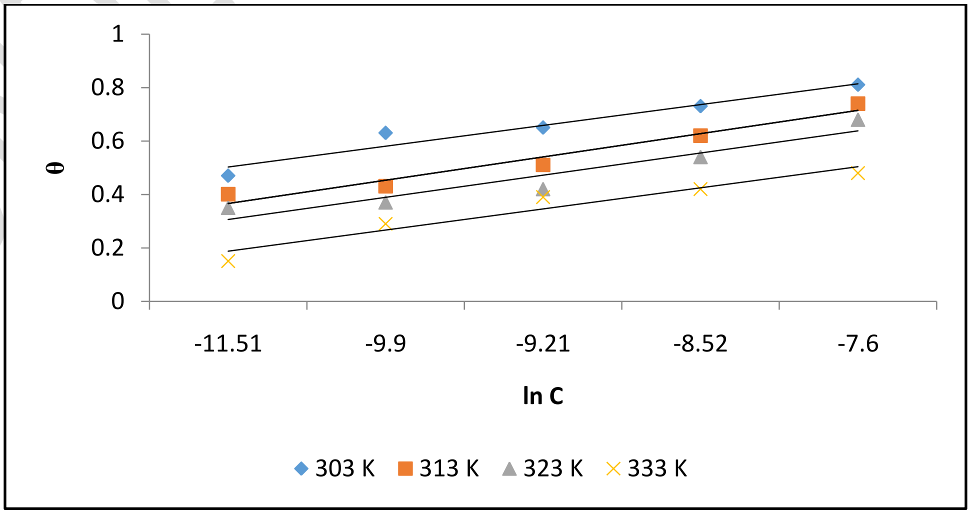


Figure 3: Temkin adsorption isotherm for mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of Mb4.

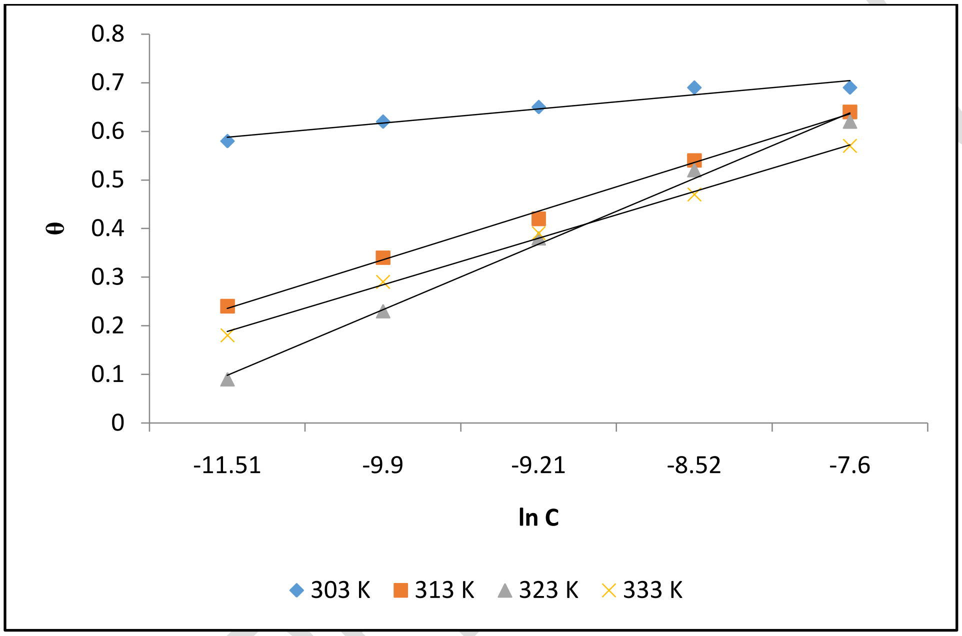


Figure 4: Temkin adsorption isotherm for mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of Mb5.

Table 3: Some adsorption parameters from Temkin isotherm for mild steel coupons in 1 M HCl containing different concentrations of Mb4 and Mb5 at 303 – 333 K.

Inhibitor	Temp. (K)	K_{ads} (L g^{-1})	f	- a	-ΔG^{o}_{ads} (kJ/mol)	R^2
Mb4	303	134.67	11.90	5.95	22.47	0.949
	313	14.67	11.49	5.75	18.80	0.958
	323	14.69	12.05	6.03	18.00	0.902

	333	3.97	12.66	6.33	14.94	0.932
Mb5	303	$2.33\text{x}10^8$	34.48	17.24	92.52	0.942
	313	3.90	10.00	5.00	13.99	0.996
	323	0.37	7.41	3.71	8.12	0.995
	333	2.61	10.42	5.21	13.78	0.997

In general, adsorption of the studied compounds in 1.0 M HCl onto the surface of mild steel is a spontaneous process in view of the negative values of ΔG^o_{ads} [30].

3.1.2 EFFECT OF TEMPERATURE ON INHIBITION EFFICIENCY

Corrosion rate in acidic solution is related to temperatureby the Arrhenius equation:

$$log\,\mathrm{CR} = \log \mathrm{A} - \frac{\mathrm{E_a}}{2.303\,\mathrm{RT}} \quad (8)$$

where CR is the corrosion rate evaluated from the gravimetric measurements, E_a is the energy of activation, A is the pre-exponential constant of Arrhenius, R is the molar gas constant and T the absolute temperature. Energies of activation wereobtained from the slopes of the plots of $\log CR$ versus $\frac{1}{T}$ as presented in Figures 5 and 6.

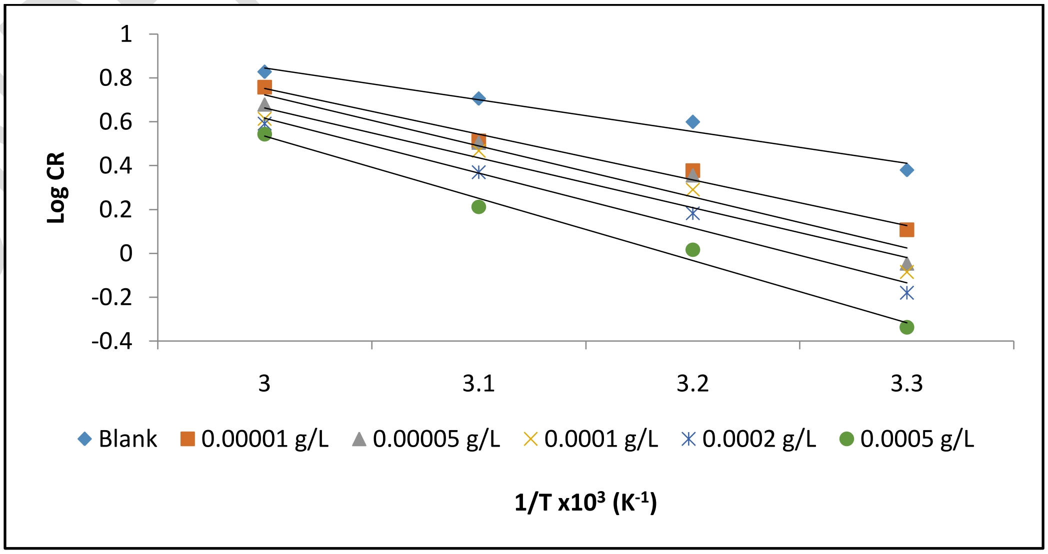


Figure 5: Arrhenius plot for mild steel coupons in 1 M HCl in the absence and presence of different concentrations of Mb4.

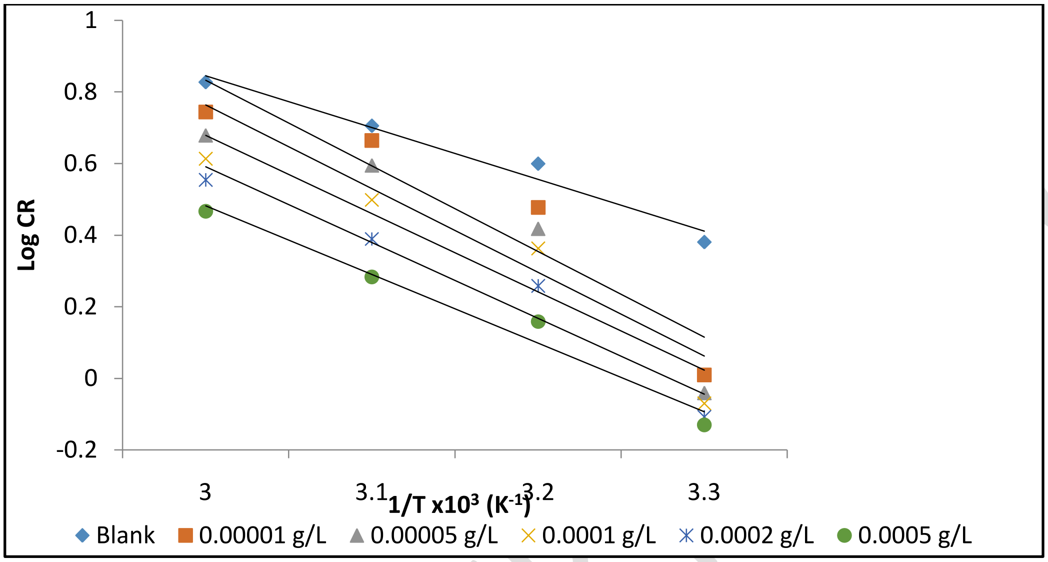


Figure 6: Arrhenius plot for mild steel coupons in 1 M HCl in the absence and presence of different concentrations of Mb5

The evaluated values of the energies of activation (E_a) are presented in Table 4. It is observed that the$E_a$values in the presence of the extracts are higher thanthe$E_a$of the blank. These values are indicative of the fact that the presence of Mb4 and Mb5 raised the energy of activation of the metal dissolution reaction. The higher values of energy of activation in the presence of Mb4 and Mb5 compared to the blank and the decrease in the percentage inhibition efficiency with increase in temperature could be attributed to physical adsorption [30]. Therefore, the mechanism of adsorption of Mb4 and Mb5 on mild steel surface is physical adsorption.

Table 4: Thermodynamic parameters for mild steel corrosion in 1 M HCl solution in the absenceand presence of different concentrations of semi-pure extracts of *C. nitida* (Mb4 andMb5) at 303 – 333 K.

Inhibitor	Concn. M x 10^{-4}	Ea (kJ mol^{-1})	ΔH^{o}_{ads} (kJ mol^{-1})	-ΔS^{o}_{ads} ($JK^{-1}mol^{-1}$)
	Blank	27.95	11.15	178.73
Mb4	0.1	29..20	16.21	163.64
	0.5	39.49	18.19	157.98
	1.0	37.97	17.67	160.03
	2.0	42.19	19.66	154.45
	5.0	47.76	22.46	146.71
	Blank	27.95	11.15	178.73
Mb5	0.1	45.38	18.76	155.35
	0.5	44.80	18.40	157.00
	1.0	41.74	17.30	160.99
	2.0	40.40	18.27	158.71
	5.0	36.76	19.95	154.33

The values of enthalpy change, ΔH^{o}_{ads}, and entropy change of adsorptions, ΔS^{o}_{ads}, were determined from the transition state equation [31]:

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{o}_{ads}}{R}\right)\exp\left(-\frac{\Delta H^{o}_{ads}}{RT}\right) \qquad (9)$$

where N is the Avogadro’s number, h is the Planck’s constant, R is the universal gas constant and T is the absolute temperature. Equation (9) is rearranged as follows:

$$ln\left(\frac{CR}{T}\right) = \left[ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{o}_{ads}}{R}\right] - \frac{\Delta H^{o}_{ads}}{RT} \quad (10)$$

Linear plots of $log(\frac{CR}{T})$ versus $\frac{1}{T}$ (Figures 7 and 8) with slopes and intercepts of $-\frac{\Delta H^{o}_{ads}}{R}$ and $\left[ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{o}_{ads}}{R}\right]$, respectively, were obtained. The slopes were used in evaluating the enthalpy change of adsorption (ΔH^{o}_{ads}) and intercepts were used in calculating the entropy change of adsorption (ΔS^{o}_{ads}) as presented in Table 4.The positive values of ΔH^{o}_{ads} indicate that the adsorption process is accompanied by adsorption of heat and it is described as endothermic.The negative values of ΔS^{o}_{ads}, are indicative of the fact that the adsorption process is associated with a decrease in entropy and this becomes the driving force for the adsorption of the studied compounds on the mild steel surface [32; 33].

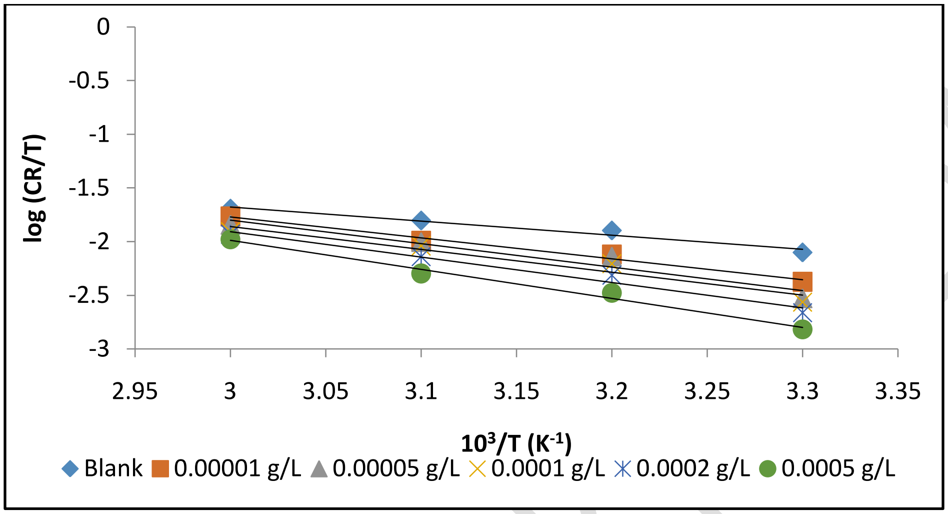


Figure 7: Ttransition state plot for mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of Mb4.

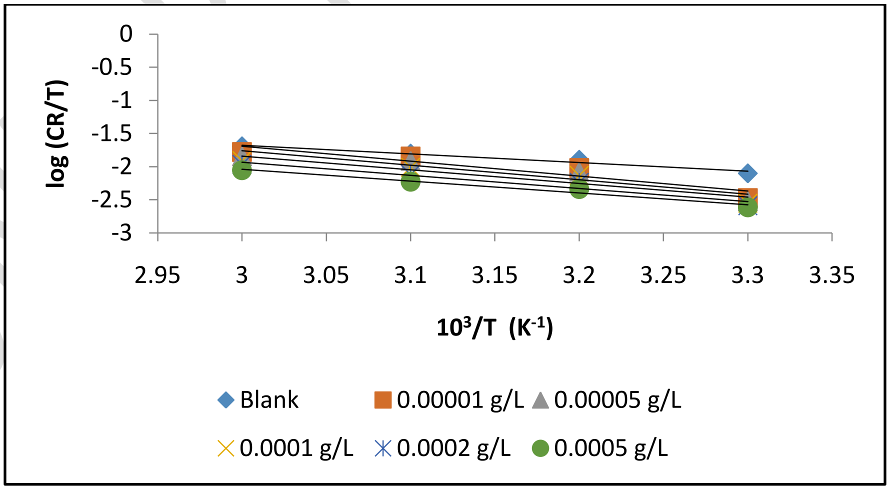


Figure 8: Ttransition state plot for mild steel corrosion in 1 M HCl solution in the absence and presence ofdifferent concentrations of Mb5.

3.3 POTENTIODYNAMIC POLARIZATION MEASUREMENTS

The presence of Mb4 and Mb5 in the test solutions pushed the cathodic and anodic regions to the minimum current magnitudes. This implies that corrosion at these regions was impeded by Mb4 and Mb5. Electrochemical parameters such as corrosion current densities (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) were generated from the Tafel plots (Figures 9 and 10) and used in the evaluation ofpercentage inhibition efficiencies (IE%) as presented in Table 5.The values of β_c and $\beta_a$were largely affected by the inclusion of Mb4 and Mb5 in the blank.When the shift in E_{corr} is higher than 85 mV, theinhibitor can be grouped as either anodic or cathodic, but if the shift is lower than 85 mV, the inhibitor may be seen as a mixed-type [34]. The potentiodynamic polarization results as presented in Table 5, where E_{corr} are in the negative and far less than the threshold value of 85 mV, revealing that Mb4 and Mb5 behavedas mixed-typecorrosion inhibitors with the inhibition of both cathodic and anodic reactions. Similar findings were reported by [35]. Furthermore, the inhibition efficiency of Mb4 (85%) is higher than that of Mb5 (69%) both at 5.0 x 10^{-4} g L^{-1} and at 303 K, indicating that Mb4 is a better inhibitor than Mb5.

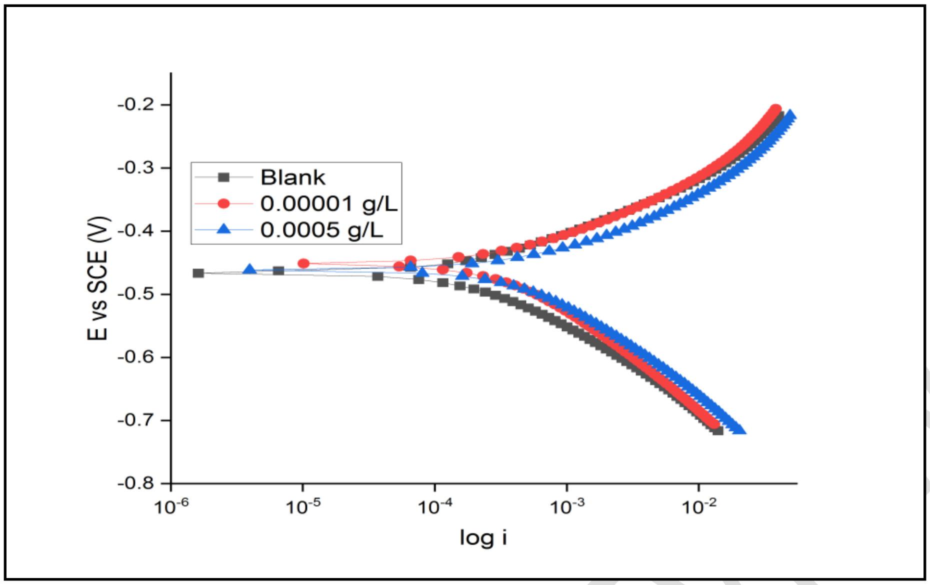


Figure 9: Polarization curve of mild steel in 1.0M HCl solution in the absence and presence of differentconcentrations of Mb4 at 303 K.

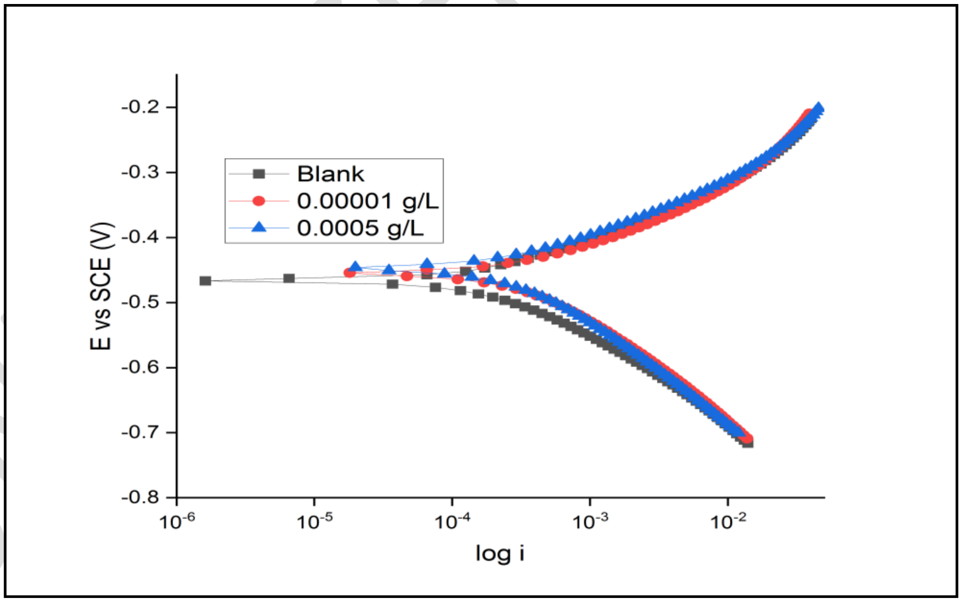


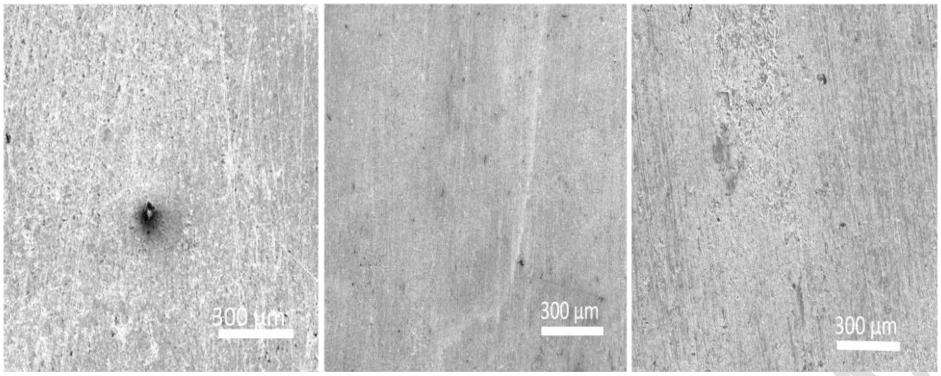
Figure 10: Polarization curve of mild steel in 1.0M HCl solution in the absence and presence of different concentrations of Mb5 at 303 K.

Table 5: Potentiodynamic polarization parameters derived from Tafel plots for mild steel immersed in 1.0M HCl in the absence and presence of different concentrations of the Mb4 and Mb5 at 303 K.

Studied compounds	Concn. (g/L)	$-E_{corr}$ (mV vs SCE)	i_{corr} (µA/cm^2)	β_c (mV dec^{-1})	β_a (mV dec^{-1})	IE%
	Blank	453.11	365.01	154	65	-
Mb4	$0.1\text{x}10^{-4}$	463.07	187.46	244	74	49
	$5\text{x}10^{-4}$	465.62	45.45	142	57	85
	Blank	453.11	365.01	154	65	-
Mb5	$0.1\text{x}10^{-4}$	464.43	176.38	125	51	52
	$5\text{x}10^{-4}$	465.96	114.75	141	97	69

3.3 SCANNING ELECTRON MICROSCOPY (SEM)

Micrographs of the mild steelcoupons immersed in 1M HCl solution in the absence and presence of the extracts were taken at a magnification of 300 µm and are presented in Figure 11 (a – c). Figure 11a revealslocalized pitting of the coupon in 1M HCl solution (blank). The roughmorphologyof mild steel in the blank is as a result of the aggressive nature of Cl^- and H^+ ions in the interfacial dissolution layer of the steel. [36;37].Similar results were reported by other workers [38; 39].The mild steel coupons in the presenceofMb4 (Figure 11b) and Mb5 (Figure 11c) are smoother than that of the blank.The differences in textural properties of the micrographs arise from the formation of dense film at the metal-solution interface by Mb4 and Mb5, hence areduction inthe substrate (mild steel) degradation rate. Additionally, Mb4 offered a better protection to the mild steel than Mb5 as seen in its micrograph (Figure 11b) being smoother than that of Mb5 (Figure 11c).



(a) (b)(c)

Figure 11: SEM image of mild steel surface exposed to (a) 1M HCl solution (blank), (b)1M HCl containing 5.0 x 10^{-4} gL^{-1} of Mb4 and (c)1M HCl containing 5.0 x 10^{-4} gL^{-1} of Mb5.

4.0 CONCLUSION

The study reveals that DCM seed extract of *C. nitida* inhibited the corrosion of mild steel in 1 M HCl solution. The inhibition efficiency was found to increase with increase in extract concentration but decreased with increase in temperature. Adsorption of the extract onto the mild steel surface fitted to Temkin adsorption isotherm. The negative values of ΔG^o_{ads} reflect the spontaneity of the corrosion inhibition process. The positive values of ΔH^o_{ads} reveal the endothermic nature of the extract adsorption process while the negative values of ΔS^o_{ads} indicate less disorder of the extract molecules on the mild steel surface and hence a stronger adsorptionof the extract molecules on mild steel surface.Mb4 and Mb5 extracts of *C. nitida*are classified as mixed-type inhibitors based on the E_{corr} values. The inhibition efficiencies obtained from gravimetric and potentiodynamic polarization methods were in agreement. The micrographs of the steel revealed formation of dense film which retarded the migration of aggressive ions in the corrodent and thus corrosion of mild steel in hydrochloric acid is inhibited by the extracts.

REFERENCES

1. James AO, Oforka NC, Abiola OK, Ita BI. A Study on the Inhibition of Mild Steel Corrosion in Hydrochloric Acid by Pyridoxol Hydrochloride. EcléticaQuímica, 2007; *32*: 31-37.

2. Karaoui M, Zarrouk A, Hsissou, R, Alami M, Assouag M. Performance of Organic Molecules as Corrosion Inhibitors for CS: A Comprehensive Review. Analytical and Bioanalytical Electrochemistry*,* 2022; *14*(6): 535-556.

3. Abakedi OU, Asuquo JE. Inhibition of mild steel Corrosion by *Micordemispuberula* leaf extract in 1 M H_2SO_4 Solution. American Chemical Science Journal, 2016;16(1): 1 - 8.

4. Akpan IA, Abakedi OU, James MA. Inhibitionof Mild Steel Corrosion in Acidic Mediumby *Telfairia occidentalis* rind extract. Asian Journal of Applied Chemistry Research, 2018; 1(3): 1–10.

5. Olawale O**,** Bello JO, Akinbami P. A Study on Corrosion Inhibitor of Mild Steel in Hydrochloric Acid using Cashew Waste. International Journal of Modern Engineering Research,2015; 5(8): 25-30.

6. Olawale O, Oyawale FA, Adediran AA, Obafemi ASCorrosion Inhibition of Mild Steel in Seawater using Jatropha Stem. *AnaleleUniversitatii - Eftimie Murgu*ll*.*Resita,2016; 23 (1): 228-238.

7. Lebe N, Georoge N, Justus N, Nneka E, Peter E. Aqueous Extracts of Roots of *Pentaclethra macrophylla,* Bentham, as eco-friendly CorrosionInhibition for Mild Steel in 0.5 M KOH Medium. International Journal of Materials and Chemistry, 2016; 6(1): 12-18.

8. Sribharathy S, Rajendran S. *Cuminum cyminum* Extracts as Eco-friendly Corrosion Inhibitor for Mild Steel in Seawater. Research Article, 2013; 1-7.

9. Kavitha N, Manjula P, Anandha Kumar N. Syneristic Effect of Papaya Leaves Extract-Zn^{2+}in Corrosion Inhibition of Mild Steel in Aqueous Medium. Research Journal of Chemical Science*,* 2014; 4 (8): 88-93.

10. Abakedi OU, Ekpo VF, John EE. Corrosion Inhibition of Mild Steel by *Stachytarphetaindica* leaf extract in Acid Solution. The Pharmaceutical and Chemical Journal, 2016; 3(1): 165-171.

11. Ratsch C. The Encyclopedia of Psychoactive plants*:*Ethno-pharmacology and its applications. Foreword Publisher, accessed 26th November, 2005.

12. Kanoma AI, Muhammad I, Abdullahi S, Shehu K, Maishanu HM, Isah AD.Qualitative and Quantitative Phytochemical Screening of Cola Nuts (*Cola Nitida and Cola Acuminata*). Journal of Biology, Agriculture and Healthcare,2014; 4 (5): 2224-3208.

13. Duke JA. Handbook of Nuts. Boca Raton, Fe: CRC Press; p.343; 2001

14. Benjamin LT, Rogers AM, Rosenbaum A. Coca cola Deficiency Harry Holingrowthand the chattanoogatrial of 1991. J histolBehavioural Sci.1991; 27(1):42-45.

15. Blades MG. Functional Foods or Neutraceutical. Nutrition and Food Science, 2000; 30(2): 73-75.
16. National Association of Corrosion Engineers NACE). Corrosion Basics. An Introduction – official NACE publication, Finland, pp.34-40; 2000

17. Obot IB, Obi-Egbedi NO. Fluconazole as an Inhibitor for Aluminium Corrosion 0.1 M HCl. Colloid Surface: Physio-chemistry.Engineering Aspects,2008; 330: 207-212.

18. Nabuk OE, Ebenso EE, Ibok UJ.Adsorption, Synergistic Inhibitive Effect and Quantum Chemical Studies of Ampicillin (AMP) and Halides for the Corrosion of Mild Steel in H_2SO_4. Journal of Applied Electrochemistry, 2010; 40, 445-456.

19. Roy P, Sukul D. Protein-surfactant Aggregate as Potential Corrosion Inhibitor for Mild Steel in Sulphuric Acid: zein-SDS system. Royal Society of Chemistry Advances, 2915; 5: 1359-1365.

20. Tsuru T, Haruyama S, Gijutsu B. The Principle of Corrosion and the Mathematical Analysis of Experimental Results. Japan Society of Corrosion Engineers,1978;27: 573-578.

21. Garai S, Garai S, Jaiasankai P, Singh JK, Elango A. (2012). A Comprehensive Study on Crude Methanolic Extract of *Artemisia pallens* (Asteraceace) and its Actives Component as Effective Corrosion Inhibitors of Mild Steel in Acid Solution. Corrosion Science,2012;60: 193-204.

22. Loto CA, Popoola API. Technical Report: Effect of *Cola Acuminata*.International Journal of Electrochemical Science,2012; 7: 2983–2996.

23. Akpan IA,Offiong NO. Electrochemical and Gravimetric Studies of the Corrosion Inhibition of Mild Steel in HCl Medium by Cephalexin Drug. American Journal of Chemistry and Material Science, 2014;1(1): 1-6.

24. Bhat JI, Alva VDP. Inhibition Effect of Miconazole Nitrate on the Corrosion of Mild Steel in Hydrochloric Acid Medium. International Journal of Electrochemistry,2011;406: 1- 8.

25. Umoren SA. Inhibition of Aluminium and Mild steel Corrosion in Acidic Medium using Gum Arabic. Cellulose,2008; 15: 751 – 761.

26. Subha R, Saratha R. Naturally occurring substance (*cahendulaoffinalis* flower) as a Corrosion Inhibitor of Mild Steel in 1.0 HCl. Corrosion Science,2006; 53: 556-562.

27. Abd El-Rehim SS, Ibrahim AM, Khalid KF. The Inhibition of 4-(2^1-amino-5^1-methylphenylazo)antipyridine on Corrosion of Mild Steel in HCl solution. Materials Chemistry and Physics,2001; 70: 268 – 273.

28. Fiala A, Chibani A, Darchen R, Boulkamh A, Djebbar K. Acetylacetone Complexes as new Corrosion Inhibitor in Phosphoric Media: Inhibition and Synergism Study. Applied Surface Science,2007; 253: 9347 – 9351.

29. Abdullah A, Hameed KW. Transition State Theory and Reaction Kinetic for the Corrosion of Steel in Acid Media. AL-Fatih Journal,2008; 35: 1 – 9.

30. Umoren SA, Eduok UM, Oguzie EE. Corrosion Inhibition of Mild Steel in 1 M H_2SO_4 by Polyvinyl Pyrrolidone and Synergistic Iodide Additives. PortugaliaeElectrochemica Acta,2008; 26(6): 533 – 546.

31. Emranuzzaman T, Kumar S,Vishwanatham G. Synergistic Effects of Formaldehyde and Alcoholic Extract of Plant Leaves for Protection of N80 Steel in 15% HCl. Corrosion Engineering, Science and Technology,2004; 39,327 – 332.

32. Xianghong LI, Shuduan D, Hui FU, Guannan MU.Inhibition Effect of 6-Benzylaminopurine on the Corrosion Cold Rolled Steel in H_2SO_4 Solution. Corrosion Science, 2009;33: 303 – 343.

33. Sahakitpichan P, Mahidol C, DisadeeW, Ruchirawat S, Kanchanapoom T. Unusual glycosides of pyrrole alkaloid and 4'-hydroxyphenyl ethanamide from leaves of *Moringa oliefera*. Phytochem. 2011; 72: 791–795.

34. Loto RT, LotoCA, Popoola AP. Inhibition Effect of Deanol on Mild Steel Corrosion in Dilute Sulphuric Acid.S. Afr. J. Chem. 2015;68: 105–114.

35. Dehghani A, Bahlakeh G, Ramezanzadeh B, Ramezanzadeh M. Potentials of Borage Flower Aqueous Extract as an Environmentally Sustainable Corrosion Inhibitor for Acid Corrosion of Mild Steel: Electrochemical and Theoretical.J. Mol. Liq. 2019; 277: 895 – 911.

36. Loto CA, Loto RT, Olufunmilayo OJ. Effect of Benzamide on the Corrosion Inhibition of Mild Steel in Sulphuric Acid.S. Afr. J. Chem., 2017; 70: 38–43.

37. Anadebe VC, Nnaji PC, Okafor NA, Ezeugo JO, Abeng FE, Onukw OD. Evaluation of Bitter Kola Leaf Extract as an Anticorrosion Additive for Mild Steel in 1.2 M H_2SO_4Electrolyte. S. Afr. J. Chem.,2021; 75: 6–17.

38. Al-Bataineh N, Al-Qudah AA, Abu-Orabi S, Bataineh T, Hamaideh RS, Al-Momani IF, Hijazi AK. Use of *Capparis decdua* Extract as a Green Inhibitor for Pure Aluminium Corrosion in Acidic Media. Corrosion Science and Technology, 2022; 21(1): 9-20.

39. Olawale O**,** Bello JO, Akinbami P. A Study on Corrosion Inhibitor of Mild Steel in Hydrochloric Acid using Cashew Waste. International Journal of Modern Engineering Research,2015; 5(8): 25-30.