Synsepalum dulcificum Leaves Extract as Green Inhibitor for Mild Steel Corrosion in Hydrochloric Acid

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ABSTRACT

Corrosion inhibition efficiency of *Synsepalum dulcificum* leaves extract for mild steel (mls) in 1.0 M HCl was evaluated by electrochemical and gravimetric methods. The results of the studies showed that *S. dulcificum* has good inhibitive properties with inhibition efficiency (% I) reaching 94 at 1000 ppm inhibitor concentration. The enthalpy was negative (which indicated the exothermic nature of adsorption of *S. Dulcificum*) and decreased steadily from -25.28 kJ/mol at 100 ppm to -34.41 kJ/mol at 1000 ppm *S. dulcificum* concentration. Values of the Gibbs free energy were negative (ΔG_{ads} = -13.41 kJ/mol at 303 K and -17.32 kJ/mol at 343 K) suggesting spontaneous adhesion of the *S. dulcificum* molecules on the surface of mls. The adsorption of *S. dulcificum* conformed to the Langmuir isotherm model and values of ΔG_{ads} also suggested that adsorption of S. *dulcificum* was physisorptive since values of ΔG_{ads} up to -20 kJ/mol are consistent with physical adsorption. The results of the studies revealed that activation energy increased with increase in *S. dulcificum* concentration which indicated that the energy required for corrosion of mls increased in the presence of *S. dulcificum* extract. Potentiodynamic Polarization studies revealed that *S. dulcificum* functions as mixed type inhibitor since values of corrosion potential (E_{corr}) increased on addition of *S. dulcificum* with no particular trend. Electrochemical impedance spectroscopy (EIS) analysis revealed that charge transfer resistance (R_{ct}) increased as *S. dulcificum* concentration increased to reach 1413.3 Ω cm^2 at 1000 ppm.

Keywords: Corrosion Inhibition, Electrochemical methods, Inhibition Efficiency, Mild Steel, *Synsepalum dulcificum*

INTRODUCTION

The corrosion of steel is a major industrial challenge that has stimulated quite a number of researches (Udhayakala, 2015). Solutions of acid are extensively employed in industries, with essential areas of relevance such as acid pickling of steel, oil well acidification, and processing of ore. These acid solutions cause deterioration of steel due to its aggressiveness (Saqalli *et al*., 2017). The utilization of corrosion inhibitors is a largely practical, cost-effective and simple method for preventing the acid corrosion of steel (Foulda *et al*., 2014).

Extracts from plants have been investigated and outlined by numerous authors as potential corrosion inhibitors in various media that are aggressive and this has been linked to the presence of phyto-compounds present in them (Ebenso *et al*., 2008). Phyto-compounds containing functionalities that are rich in electrons such as Oxygen (O) Nitrogen (N), sulphur (S) atoms, aromatic and heterocyclic rings, multiple bonds, act as efficient corrosion inhibitors (Osabor *et al*., 2016). The use of plant materials has continued to receive attention as suitable replacement for

synthetic inhibitors. The overwhelming interest on plant materials can be attributed to the reality that they are inexpensive, environmentally pleasant and readily available (Umoren *et al*., 2011).

Synsepalum dulcificum is native to tropical West Africa. It is known as Igbayun among the Yoruba people, Mkpatun by the Ibibio and Efik people of Akwa Ibom and Cross Rivers States and Azimomo by the Benin people of Edo State. The leaves contains rhamnose, arabinose, galactose, glucose and xylose among other compounds (Huajun *et al*., 2017). The leaves are thin, papery, leathering and ever green (Inglet *et al*., 1965; Behpour *et al*., 2011)**.** This research was premeditated to investigate the inhibitory consequence of *S. dulcificum* on the corrosion of mls in hydrochloric acid medium by gravimetric and electrochemical techniques.

MATERIALS AND METHODS
Sampling, extraction procedure and preparations

Mls sheet employed for this investigation was obtained commercially in an open market from Uyo, Akwa Ibom state, Nigeria. The mls obtained

was mechanically press-cut into 4 cm x 4 cm coupons. The coupons were then cleaned with emery paper, degreased in ethanol, immersed in acetone, dried at room temperature and kept in a desiccator preceding use.

The *S. dulcificum* leaves used for this study were obtained from Ibadan, Oyo State, Nigeria and were thoroughly washed, dried and pulverized into powder. 214 g of the powder was obtained and soaked in 250 mL of methanol at room temperature for 72 h. The mixture was then sifted and the filtrate was concentrated by a rotary evaporator to remove the excess solvent (Umoren *et al.*, 2011).

Test solutions were prepared in the concentration range of 100 –1000 pm by diluting the stock solution with specific volumes of 1.0 M HCl (Umoren *et al.*, 2011).

Weight loss (Gravimetric) method

Coupons were accurately weighed and immersed in beakers containing hydrochloric acid and different concentrations of the inhibitor test solutions. The coupons were then retrieved from the test solutions after 5 hours, immersed in NaOH/Zinc dust solution, washed carefully in solution of detergent, doused in double refined water and then in acetone, dried in air then finally weighed (Odozi *et al*, 2019). This was repeated at different temperatures (303K, 313K, 323K, 333K and 343K) using a thermostated water bath. The corrosion rates (CR), %I and other parameters were then computed using the relationships presented in equations 1-3 (Kumpawak *et al.*, 2012; Fouda *et al.*, 2013; Nwosu *et al.*, 2016).

$$\text{CR (gcm}^{-2}\text{h}^{-1}) = \frac{87.6(Wo - W1)}{A \times d \times t} \qquad (1)$$

$$\%I = \left(\frac{CR_{blan\,k} - CR_{inh}}{CR_{blank}}\right) \times 100 \qquad (2)$$

$$\theta = \frac{\%I}{100} \qquad (3)$$

Where A = area of specimen, t = time of immersion (hours), W_o = weight of coupon before immersion, W_1 = weight of coupon after immersion, CR = corrosion rate and d = metal density which is 7.86 g/cm^3.

Electrochemical investigation

The Princeton applied electrochemical workstation was employed for all electrochemical measurements. Electrochemical cell is comprised of three electrodes (with platinum as the counter electrode, saturated calomel electrode (SCE) as reference electrode, and the mild steel as working electrode). Measurements were made after the system was allowed to reach steady open circuit potential (OCP) of between 0 and 1800 s (Olasunkanmi *et al*, 2016). EIS was executed at frequency of 10 kHz to 10 mHz at room temperature. Polarization measurements were performed between -0.15 V to +0.15 V vs. E_{OC} at a scan rate of 0.2 mV/s. Experiments were conducted in 1.0 M hydrochloric acid, in the absence and presence of 100 ppm, 500 ppm and 1000 ppm of the plant extracts. The data generated were analyzed by means of Nyquist (Figure 4) and Tafel (Figure 5) plots. Inhibition efficiency was computed with the aid of equation 4 using charge transfer resistance values obtained. Values of constant phase element, CPE (Y_o) and charge transfer resistance (R_{ct}) were employed to compute the double layer capacitance(C_{dl}) of the adsorbed film using equation 5. Inhibition efficiency was also computed using corrosion current densities (I$_{corr}$) obtained from analyses of the Tafel plots (Umoren *et al.*, 2011).

$$\varepsilon_{EIS} = 100\left(\frac{R_{ctI} - R_{ctB}}{R_{ctI}}\right) \qquad (4)$$

$$C_{dl} = (Y_0\,R_{ct}{}^{n-1})^{\frac{1}{n}} \qquad (5)$$

$$\varepsilon_{PD} = 100(1 - \frac{I_{corr}^i}{I_{corr}^b}) \qquad (6)$$

where R_{ctB} = charge transfer resistance in the free acid and R_{ctI} = charge transfer resistance in the presence of *S. dulcificum* . I_{corr}^b = corrosion current density in the presence *S. dulcificum* and I_{corr}^i = corrosion current density in the absence of *S. dulcificum* , n = constant (level of roughness of mls surface).

RESULTS AND DISCUSSIONS
Weight loss

CR, %I and surface coverage for mls in 1M hydrochloric acid solution at 303 K, 313 K, 323 K, 333K and 343 K in the presence and absence of *S. dulcificum* is presented in Table 1. It is evident from the values presented on Table 1 that CR decreased as *S. dulcificum* concentration increased. This suggest an increased number of adsorbed molecules of *S. dulcificum* constituents on the mls surface, thus decreasing the corrosion rate. The values for %I on Table 1 improved with increase in *S. dulcificum* concentration. %I also decreased with increase in temperature which suggests possible desorption of some of the adsorbed molecules of *S. Dulcificum* on the steel surface (Umoren *et al.*, 2011; Ituen *et al.*, 2017; Sigircik *et al.*, 2015). Plots of C/θ vs. C for adsorption of the *S. dulcificum* on mls surface in 1 M hydrochloric acid are presented in Figure 1. Adsorption of *S. dulcificum* on mls surface obeys Langmuir isothermΔG $_{ads}$ was determined from equation 8 and the results together with other parameters obtained from Langmuir plots are presented in Table 2. Values of ΔG$_{ads}$ presented in Table 2 suggests that adsorption of components of the inhibitor on mls surface occurred by physical

adsorption since values of ΔG_{ads} up to -20 kJ/mol are consistent with physical adsorption ((Umoren *et al*., 2011). The result also indicates spontaneous adsorption since values of ΔG_{ads} are negative. Change in enthalpy (ΔH) and change in entropy (ΔS) were determined from the transition state plot

(Figure 3, Table 3). Negative ΔH suggests exothermic nature of steel dissolution process. ΔS values narrowed as *S. dulcificum* concentration increased revealing a decrease in disordering on going from reactant to the activated complex (Akbarzadeh *et al*., 2011).

Table 1: Calculated values of corrosion rate, inhibition efficiency and surface coverage

Temperature (K)	Inhibitor Concentration (ppm)	$CR \times 10^{-4}$	$(gcm^{-2}h^{-1})$	%I	Θ
	Blank	33.30		-	-
	100	8.06		75.8	0.758
	300	4.43		86.7	0.867
303	500	2.34		92.9	0.929
	800	2.20		93.4	0.934
	1000	1.70		94.9	0.949
	Blank	107.30		-	-
	100	34.98		67.4	0.674
	300	26.93		74.9	0.749
313	500	11.59		89.2	0.892
	800	11.37		89.4	0.894
	1000	10.51		90.2	0.902
	Blank	201.07		-	-
	100	99.91		50.3	0.503
	300	91.26		54.6	0.546
323	500	85.03		57.7	0.577
	800	63.32		68.5	0.685
	1000	47.03		76.6	0.766
	Blank	258.30		-	-
	100	143.96		44.2	0.442
	300	125.65		51.3	0.513
333	500	121.26		53.0	0.530
	800	99.85		61.3	0.613
	1000	83.59		67.6	0.676
	Blank	276.06		-	-
	100	168.12		39.1	0.391
	300	162.05		41.3	0.413
343	500	148.80		46.1	0.461
	800	141.07		48.9	0.489
	1000	128.64		53.4	0.534

The activation energy (Ea) values were determined from Arrhenius plots (Figure 2) for mild steel

corrosion using equation 10 (Andreani *et al*., 2016).

Table 2: Parameters obtained from Langmuir plots

Temperature (K)	R^2	ΔG_{ads} (kJ/mol)
303	0.999	-13.41
313	0.997	-14.41
323	0.999	-15.21
333	0.991	-16.23
343	0.995	-17.32

Collision must occur between both species involved for the acid to cause dissolution of the mls surface. Acid molecules must have energy equivalent to the E_a^{HCl} on collision with the mls surface. According to the results presented in Table 3, higher E_a^{HCl} can be visibly observed with

inhibited solution than E_a^{HCl} which suggest that introduction of *S. dulcificum* increased the energy obstacle that acid molecules must overcome in other to succeed in corroding the mls surface (Ituen *et al*., 2017).
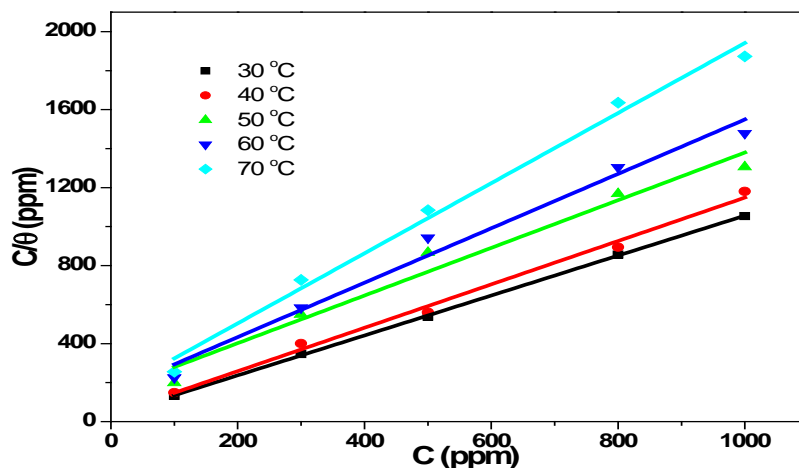
Figure 1: Langmuir plots for corrosion of mild steel in 1 M HCl in the absence and presence of *S. dulcificum* extract at temperature range of 303 K – 343 K

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (7)$$

$$\Delta G_{ads} = -RT\ln(55.5\,K_{ads}) \qquad (8)$$

$$Log\,\frac{CR}{T} = \left[Log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303\,R}\right) \right] - \left(\frac{\Delta H}{2.303\,RT}\right) \quad (9)$$

$$Log\,CR = Log\,A - \frac{E_a}{2.303\,RT} \qquad (10)$$

Where h = Planck's constant, R = molar gas constant, K is adsorption constant, E_a is activation energy, A = Arrhenius pre-exponential constant.

Table 3: Thermodynamic Parameters obtained from Arrhenius and Transition State plots

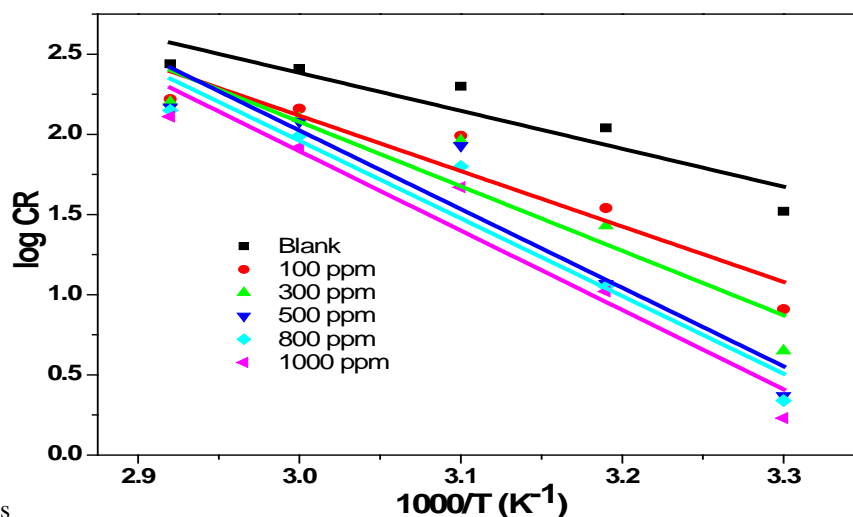| Solution	Ea (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
Blank	45.5	-14.26	0.22
100 ppm	66.1	-25.28	0.21
300 ppm	76.9	-27.13	0.20
500 ppm	93.8	-31.02	0.18
800 ppm	92.7	-31.45	0.17
1000 ppm	94.8	-34.41	0.16

Figure 2: Arrhenius plots for mls corrosion in 1 M HCl in the absence and presence of *S. dulcificum* at a temperature range of 303 K – 343 K
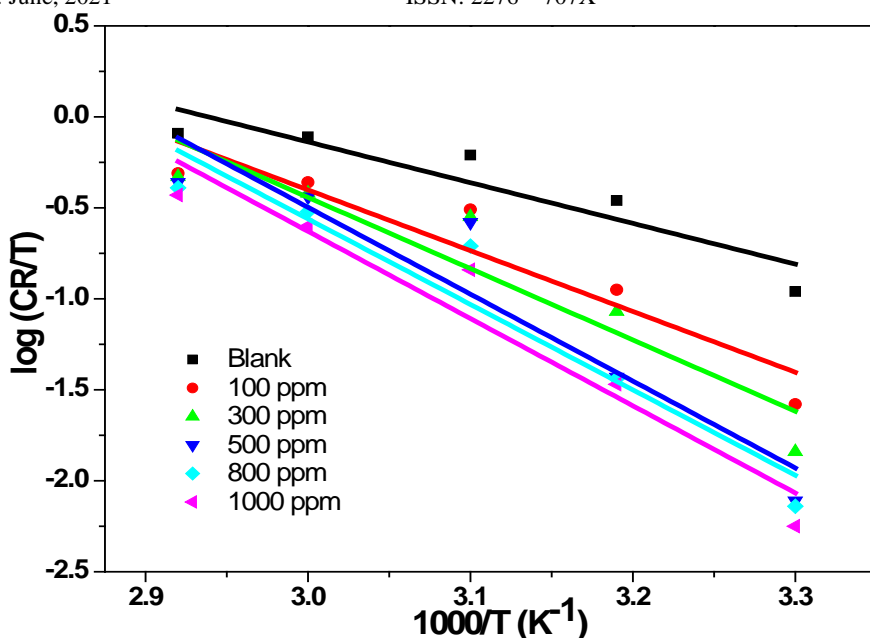
Figure 3: Transition state plots for corrosion of mls in 1 M HCl in the absence and presence of *S. dulcificum* at a temperature range of 303 K – 343 K

Electrochemical impedance spectroscopy (EIS)

The Nyquist plots for hydrochloric acid corrosion of mls in the presence and absence of *S. dulcificum* are presented in Figure 4. It was observed that the Nyquist impedance arcs widen as *S. dulcificum* concentration increased. The width of the curves increased as *S. dulcificum* concentration rises indicating increased steel surface coverage. The imperfections in curves of the Nyquist impedance semicircles could be due to surface roughness or mls surface inhomogeneity (Ituen *et al.*, 2017; Yurt *et al.*, 2006).
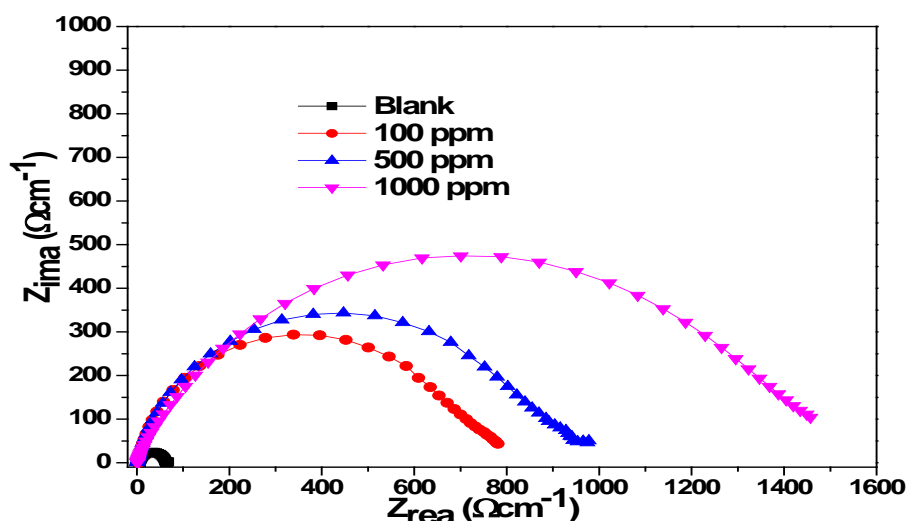

Figure 4: Nyquist plots for the corrosion of mls in 1 M HCl in the absence and presence of different concentrations of *S. dulcificum*

Impedance parameters such as R_{ct} and C_{dl} were determined from Nyquist plots and are presented in Table 4. R_{ct} increased with increase in *S. dulcificum* concentration which suggests an increase in the %I of corrosion. The decreasing values of C_{dl} may be due to adsorption of *S. dulcificum* on the surface of mls.

Table 4: Electrochemical Impedance Parameters for mls in 1M hydrochloric acid in the absence and presence of *S. dulcificum*

Blank/inhibitor concentrations	R_s (Ωcm^2)	R_{ct} ($\Omega\ cm^2$)	N	Y_o($\mu\Omega^{-1}s^n cm^{-2}$)	C_{dl} (μFcm^{-2})	%I
Blank	0.983	56.2	0.886	155.8	14.2	-
100 ppm	0.997	788.5	0.892	120.3	11.6	92.9
500 ppm	1.112	992.7	0.897	112.8	6.2	94.3
1000 ppm	1.018	1413.3	0.889	98.7	3.4	96.0

The heterogeneity of the surface is compensated for by CPE in the equivalent circuit with magnitude given by Y_0 and n. The values of n signify abnormality of the constant phase element and may be employed to envisage the level of heterogeneity or roughness of the mls surface. It increased on introduction of *S. dulcificum* indicating that the surface coarseness of the mls is reduced by adsorption of *S. dulcificum* (Geethajali and Subhashini, 2015). When n=1, Y_0 is capacitive; when n =-1, Y_0 is inductive; when n= 0.5, Y_0 is Warburg impedance (Geethajali and Subhashini, 2015). Since n is in between these values, the obtained n values suggests relative and/or integrated influence of above factors such that it is not just a single resistance, inductive element or capacitance. Another significance of values of n is deviation from ideal behaviour or phase shift; it

increases on addition of inhibitor, which suggests formation of passive film on the surface of mls, and is liable for the decrease in corrosion rates. This is also evident in the obtained values of charge transfer resistances, which increased with increase in concentration of *S. dulcificum* than in the absence of *S. dulcificum*, thus indicating that retardation of mls corrosion rate by *S. dulcificum* is concentration dependent.

Potentio-dynamic polarization (PDP) measurement

The equations for the reactions expected at the anode and cathode are stated thus:

Anode: Me $\rightarrow$ Me^{2+} + 2e   (11)

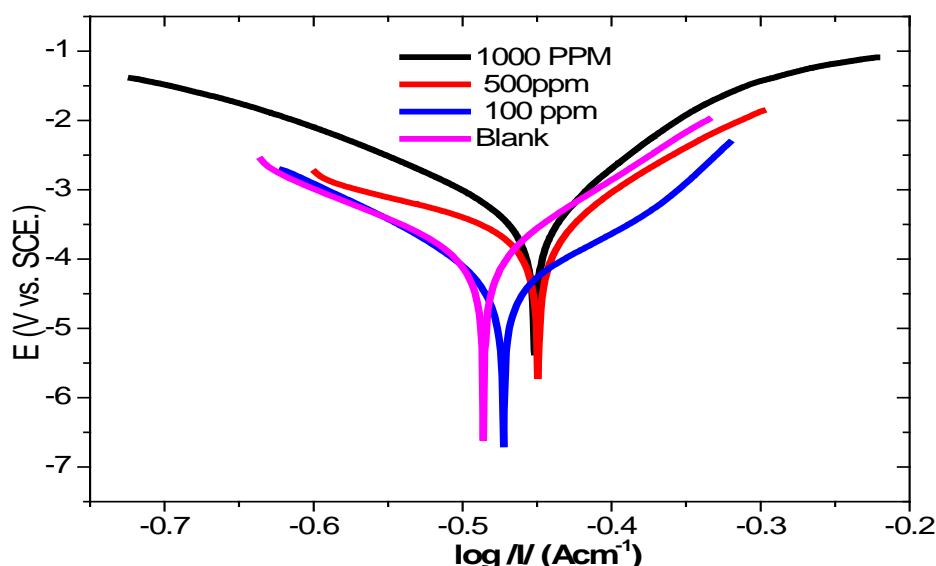Cathode: 2H$^+$ + 2e $\rightarrow$ H$_2$ (12)

Figure 5: Tafel plots for mls in 1 M HCl in absence and presence of *S. dulcificum*.

Table 5: Parameters obtained from Potentiodynamic Polarization measurement

Blank/inhibitor Concentrations	β_a (mVdec^{-1})	β_c (mVdec^{-1})	I_{corr} (μAcm^{-2})	E_{corr} (mV/SCE)	ε_{PDP} (%)
Blank	66.8	84.5	951.1	-498	-
100 ppm	94.2	85.6	131.8	-482	86.1
500 ppm	91.6	90.3	122.4	-483	87.1
1000 ppm	94.9	79.6	104.6	-482	89.0

Oxidation of metal at the anode leads to corrosion of metal and H$_2$ gas is released at the cathode as shown in equations 11 and 12.

The corrosion potential (E_{corr}), corrosion current densities (I_{corr}), Tafel cathodic and anodic constants (β_c and β_a) and the ε_{PDP}(%) obtained from PDP measurements are presented in Table 5. In the presence of *S. dulcificum* , the values of I_{corr} dropped to lower current regions as the concentration of *S. dulcificum* increased while E_{corr} increased on addition of *S. dulcificum* with no particular trend . This indicates decrease of mls corrosion in the presence of *S. dulcificum* . An inhibitor with E$_{corr}$ values in this manner is regarded as a mixed type inhibitor with anodic prevalence (Odozi *et al*, 2019). The values of Tafel cathodic and anodic constants obtained exhibited slight difference in the presence of the inhibitor with no trend. The computed ε_{PDP}(%) increased with increase in concentration of *S. dulcificum* (Geethajali and Subhashini, 2015; Mourya *et al.*, 2015).

CONCLUSION

Gravimetric and electrochemical measurement results obtained for the use of *S. dulcificum* extract as corrosion inhibitor are in good agreement and revealed the efficacy of *S. dulcificum* leave extract for the corrosion inhibition of mild steel in hydrochloric acid. Percentage inhibition efficiency of *S. dulcificum* depended on temperature and its addition resulted to higher activation energy. Charge transfer resistance increased with increase in concentration of *S. Dulcificum*. PDP result showed that *S. dulcificum* is a mixed-type inhibitor.

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