



Mild steel corrosion inhibition by *Microdesmis puberula* root extract in acidic medium

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Abstract

The corrosion inhibition of mild steel in 1 M H₂SO₄ solution by *Microdesmis puberula* root extract has been studied using weight loss and hydrogen evolution methods. The data obtained revealed that the inhibition efficiency increased with increase in extract concentration up to 4 g/L, before decreasing at 5 g/L. An increase in temperature led to a decrease in the inhibition efficiency by the extract. The adsorption of *Microdesmis puberula* root extract on mild steel surface obeyed Freundlich adsorption isotherm and occurred spontaneously. Physical adsorption has been proposed for the adsorption of *Microdesmis puberula* root extract on mild steel surface. The activation energy and other thermodynamic parameters for the inhibition process have been calculated and discussed.

Keywords: *microdesmis puberula*, mild steel, freundlich isotherm, extract, corrosion inhibition

1. Introduction

Research on the discovery or formulation of efficient inhibitors to reduce the corrosion of metals in aggressive environments will continue to attract much attention globally, since metals are valuable materials used for the construction of both domestic and industrial appliances and equipment. Although several inorganic and synthesized organic compounds have been in use as efficient inhibitors for mild steel corrosion for decades, their usage nowadays is limited. The major drawback being the issue of biotoxicity^[1, 2]. This has led researchers to finding another class of inhibitors which should be efficient, environmentally-friendly as well as being non-toxic. A major breakthrough in this regard came with the extraction of green inhibitors from natural products. Some root extracts have been reported as potential inhibitors of mild steel corrosion in acidic medium^[3-7].

Microdesmis puberula plant (Ibibio name: Ntabit) belongs to the family Pandaceae. Its leaves are used as a fodder for goats. The herbal medicinal uses of parts of *Microdesmis puberula* in Nigeria have been reported^[8, 9]. The phytochemical analysis of *Microdesmis puberula* root extract revealed the presence of saponins, cardiac glycosides, deoxy sugars, terpenes and alkaloids^[10]. The active components isolated from *Microdesmis puberula* root extract include spermine and spermidine derivatives^[11]. Previous studies^[12] reported the effectiveness of *Microdesmis puberula* leaf extract as mild steel corrosion inhibitor in acidic medium. The aim of this research was to assess the inhibition efficiency of *Microdesmis puberula* root extract on mild steel corrosion in H₂SO₄ solution.

2. Materials and Methods

2.1 Test Materials

The chemical composition of the mild steel used for this work was (weight %): C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09) and Fe (98.83). The sheet was mechanically press - cut

into 4 cm x 5 cm coupons, and polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dipped in acetone before air-drying. They were then stored in a moisture - free desiccator before use in corrosion studies.

2.2 Preparation of *Microdesmis puberula* root extract

Fresh roots of *Microdesmis puberula* were collected from a bush in Uruan, Akwa Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria. They were washed, cut into small pieces and air - dried at 30°C for seven days. They were then ground to powder. *Microdesmis puberula* ethanol root extract was obtained according to a method described previously^[13].

2.3 Weight loss method

Mild steel coupons which had previously been cleaned and weighed were suspended with the aid of glass hooks and rods and immersed in 100 cm³ of 1 M H₂SO₄ solution (blank) and in 1 M H₂SO₄ solution containing 1.0 g/L - 5.0 g/L *Microdesmis puberula* root extract (inhibitor) in open beakers. In each experiment, one mild steel coupon per beaker was used. The beakers were then placed in a thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C, respectively. The mild steel coupons were retrieved from the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing.

The inhibition efficiency by the weight loss method I_{WL}(%) was obtained using the equation^[14]:

$$I_{WL}(\%) = \left(\frac{W_0 - W_1}{W_0} \right) \times 100 \quad (1)$$

Where W₀ is the weight loss of the mild steel coupon in the

absence of the extract (blank) and W_1 is the weight loss of the mild steel coupon in the presence of extract.

The corrosion rate (CR) of mild steel in 1 M H_2SO_4 solution was calculated using the formula:

$$CR \text{ (mg cm}^{-2}\text{hr}^{-1}\text{)} = \left(\frac{W}{At} \right) \quad (2)$$

Where W is the weight loss (mg), A is the total surface area (cm^2) while t is the exposure time (hours).

2.4 Hydrogen Evolution Method

The hydrogen evolution was done following standard procedure described in literature [15]. A mild steel coupon (8.0 g) was dropped into 100 cm^3 of 1 M H_2SO_4 solution in the reaction vessel. The volume of H_2 gas evolved from the corrosion reaction was recorded every 60 seconds for 60 minutes. The same experiment was repeated in the presence of 1.0 g/L – 5.0 g/L *Microdesmis puberula* root extract in 1 M H_2SO_4 solution.

The hydrogen evolution rate (R_H) was determined through the formula [16].

$$R_H \text{ (cm}^3\text{min}^{-1}\text{)} = \frac{V_t - V_i}{t_t - V_i} \quad (3)$$

Where V_t and V_i are the volumes of hydrogen gas evolved at time t_t and t_i , respectively.

The inhibition efficiency I_{HE} (%) by the hydrogen evolution was calculated using equation (4) [17]:

$$I_{HE}(\%) = \left(\frac{R_{H0} - R_{H1}}{R_{H0}} \right) \times 100 \quad (4)$$

Where R_{H0} and R_{H1} are H_2 gas evolution rates in the absence and presence of inhibitor, respectively, at a specified time.

3. Results and Discussion

3.1 Effect of *Microdesmis puberula* root extract concentration on inhibition efficiency

Figure 1 reveals that *Microdesmis puberula* root extract concentration had a significant effect on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 solution. It can be seen that the inhibition efficiency increased with increase in *Microdesmis puberula* root extract concentration, reaching a maximum inhibition efficiency of 81.96% at 4 g/L of the extract concentration at 30°C. Figure 2 depicts the effect of *Microdesmis puberula* root extract on the volume of H_2 gas evolved in the corrosion of mild steel in 1 M H_2SO_4 . It is observed that the volume of hydrogen gas evolved in H_2SO_4 - extract medium was less than that in the blank. Furthermore, the higher the extract concentration used, the lesser the volume of H_2 gas evolved. The decrease in the hydrogen evolution rate in the presence of *Microdesmis puberula* root extract indicates the effectiveness of the extract in inhibiting the corrosion of mild steel in H_2SO_4 solution. The inhibition efficiency by the hydrogen evolution increased with increase

in the extract concentration (Table 1). The increase in inhibition efficiency with increase in extract concentration is an indication that the extract adsorbed on the metal surface, forming protective thin films which reduced the electron transfer process on the metal surface [13].

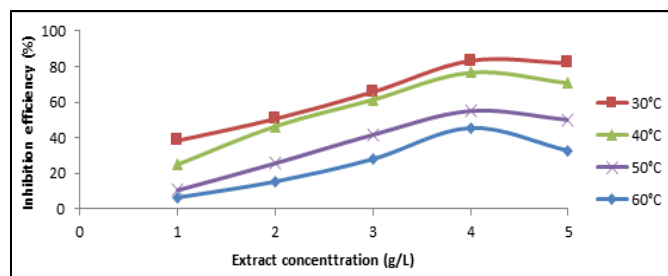


Fig 1: Effect of *Microdesmis puberula* root extract concentration on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 at different temperatures

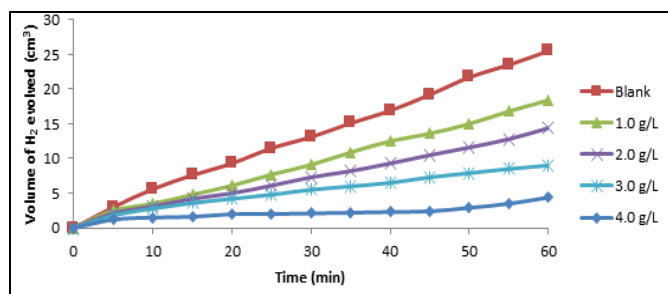


Fig 2: Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Microdesmis puberula* root extract at 30°C

Table 1: Effect of *Microdesmis puberula* root extract concentration on inhibition efficiency of mild steel in 1 M H_2SO_4 solution at 30°C (Hydrogen evolution measurements)

Extract concentration (g/L)	H_2 evolution rate ($cm^3 \text{ min}^{-1}$)	Inhibition efficiency (%)
Blank	0.425	-
1.0	0.307	27.76
2.0	0.240	43.53
3.0	0.150	64.71
4.0	0.073	82.82

3.2 Effect of temperature on inhibition efficiency

The inhibition efficiency of *Microdesmis puberula* root extract on mild steel surface was greatly affected by temperature changes. The inhibition efficiency was found to decrease with increase in temperature (Table 2). A decrease in inhibition efficiency with increase in temperature indicates that the extract functioned more effectively as an inhibitor at lower temperatures than at higher temperatures. Furthermore, physical adsorption (physisorption) of the inhibitor onto metal surface is implied when an increase in temperature leads to a decrease in the inhibition efficiency [18].

Table 2: Calculated values of corrosion rate and inhibition efficiency for mild steel corrosion in 1 M H₂SO₄ in the absence and presence of different concentrations of *Microdesmis puberula* root extract

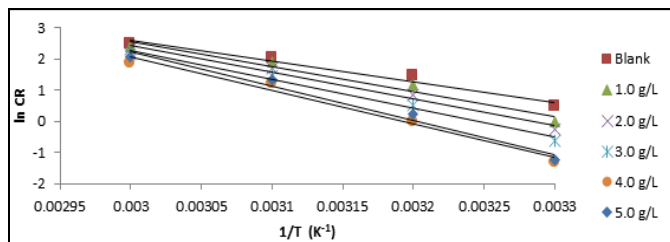
Extract conc. (g/L)	Weight loss (g)				Corrosion rate (mg cm ⁻² hr ⁻¹)				Inhibition efficiency (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	0.2550	0.6897	1.1975	1.9051	1.5938	4.3106	7.4844	11.9069	-	-	-	-
1.0	0.1570	0.5169	1.0708	1.7809	0.9813	3.2306	6.6925	11.1306	38.43	25.05	10.58	6.52
2.0	0.1259	0.3693	0.8900	1.6106	0.7869	2.3081	5.5625	10.0663	50.63	46.46	25.68	15.46
3.0	0.0874	0.2664	0.6982	1.3698	0.5463	1.6650	4.3638	8.5613	65.73	61.38	41.70	28.10
4.0	0.0427	0.1614	0.5379	1.0373	0.2669	1.0088	3.3619	6.4831	83.25	76.60	55.08	45.55
5.0	0.0460	0.2017	0.5977	1.2808	0.2875	1.2606	3.7356	8.0050	81.96	70.76	50.09	32.77

The values of the activation energy (E_a) for mild steel corrosion in 1 M H₂SO₄ solution in the presence and absence of *Microdesmis puberula* root extract were obtained using equation (5) [13].

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (5)$$

Where T is the absolute temperature, R is the universal gas constant and A is the pre-exponential factor.

From the linear plots of $\ln CR$ vs. $1/T$ (Figure 3), the activation energies (E_a) of mild steel corrosion in 1 M H₂SO₄ solution, in the absence and presence of *Microdesmis puberula* root extract, were evaluated and the results presented in Table 3. It is observed that the E_a values in the presence of the root extract were higher than the E_a value of the blank (54.75 kJ mol⁻¹). Some workers [19, 20] have attributed an increase in the E_a values in the presence of the extract compared to the blank to indicate physical adsorption while the reverse is associated with chemical adsorption. Consequently, the adsorption of *Microdesmis puberula* root extract on mild steel surface is proposed to occur by a physical adsorption process.

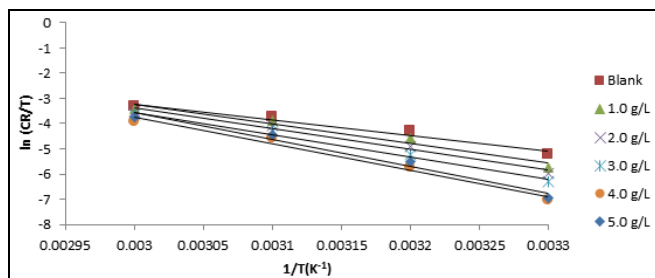
**Fig 3:** Arrhenius plot ($\ln CR$ vs. $1/T$) for mild steel corrosion in 1 M H₂SO₄ in the absence and presence of *Microdesmis puberula* root extract

The values of enthalpy of activation (ΔH°_{ads}) and entropy of activation (ΔS°_{ads}) were obtained using equation (6) [12].

$$\ln \left(\frac{CR}{T} \right) = \left[\ln \left(\frac{R}{Nh} \right) + \frac{\Delta S^\circ_{ads}}{R} \right] - \frac{\Delta H^\circ_{ads}}{RT} \quad (6)$$

Where CR is the corrosion rate, E_a is the activation energy, T is the absolute temperature, A is the Arrhenius pre-exponential factor, R is the universal gas constant, h is the Planck's constant, and N is the Avogadro's number.

The values of ΔH°_{ads} and ΔS°_{ads} presented in Table 3 were evaluated from the gradients and intercepts, respectively, of $\ln (CR/T)$ vs. $1/T$ plots (Figure 4). The positive values of ΔH°_{ads} reflect the endothermic nature of the adsorption process.

**Fig 4:** Transition state plot ($\ln (CR/T)$ vs. $1/T$) for mild steel corrosion in 1 M H₂SO₄ solution in the absence and presence of *Microdesmis puberula* root extract**Table 3:** Thermodynamic parameters for mild steel corrosion in 1 M H₂SO₄ solution in the absence and presence of *Microdesmis puberula* root extract

Extract concentration	E_a (kJ mol ⁻¹)	ΔH°_{ads} (kJ mol ⁻¹)	ΔS°_{ads} (J K ⁻¹ mol ⁻¹)
1 M H ₂ SO ₄ (Blank)	54.75	52.13	- 67.89
1.0 g/L	66.63	64.02	- 32.43
2.0 g/L	70.89	68.27	- 20.78
3.0 g/L	76.65	74.03	- 4.91
4.0 g/L	89.56	86.96	32.17
5.0 g/L	92.00	89.38	41.09

3.3 Adsorption studies

The best fit for the adsorption of *Microdesmis puberula* root extract on mild steel surface was obtained by the Freundlich isotherm defined as [21]:

$$\log \theta = n \log C + \log K_{ads} \quad (7)$$

Where C is the inhibitor concentration, θ is the degree of surface coverage, n is the interaction parameter while K_{ads} is the equilibrium adsorption constant.

Linear plot of C/θ vs. C (Figure 5) shows that the adsorption of *Microdesmis puberula* root extract on mild steel surface in 1 M H₂SO₄ solution obeyed the Langmuir adsorption isotherm. The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4.

The standard free energy of adsorption (ΔG°_{ads}) was calculated using the formula [22]:

$$\Delta G^\circ_{ads} = -RT \ln(55.5K_{ads}) \quad (8)$$

Where R is the universal gas constant, T is the absolute temperature while 55.5 is the molar concentration of water in the solution in mol dm⁻³.

The negative values of ΔG°_{ads} reveal that the mild steel

corrosion inhibition process by *Microdesmis puberula* root extract occurred spontaneously. Generally, values of $\Delta G^{\circ}_{\text{ads}}$ less negative than -20 kJ mol^{-1} indicate physical adsorption while those more negative than -40 kJ mol^{-1} indicate chemical adsorption [23, 24]. Consequently, the values of $\Delta G^{\circ}_{\text{ads}}$ obtained in this work being less negative than -20 kJ mol^{-1} coupled with a decrease in the inhibition efficiency with increase in temperature indicates a physical adsorption process.

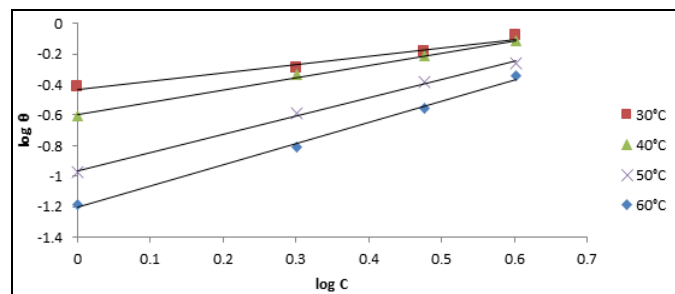


Fig 5: Plot of $\log \theta$ vs. $\log C$ (Freundlich isotherm) for mild steel corrosion in 1 M H_2SO_4 solution containing *Microdesmis puberula* root extract

Table 4: Some parameters of the linear regression of Freundlich adsorption isotherm for mild steel corrosion in 1 M H_2SO_4 solution containing *Microdesmis puberula* root extract

Temperature	R^2	n	$\log K_{\text{ads}}$	K_{ads}	$\Delta G^{\circ}_{\text{ads}}$ (kJ mol^{-1})
303K	0.9724	0.55	-0.4318	3.70×10^{-1}	-7.61
313K	0.9966	0.80	-0.5928	2.55×10^{-1}	-6.90
323K	0.9976	1.20	-0.9660	1.08×10^{-1}	-4.81
333K	0.9957	1.39	-1.2020	6.28×10^{-2}	-3.46

4. Conclusion

On the basis of this study, the following conclusions could be drawn:

1. *Microdesmis puberula* root extract appreciably inhibited the corrosion of mild steel in H_2SO_4 solution.
2. The inhibition efficiency of the extract increased with increase in extract concentration but decreased with increase in temperature.
3. Physical adsorption of *Microdesmis puberula* root extract onto the mild steel surface is proposed, based on a decrease in inhibition efficiency with increase in temperature, the activation energy in extract being greater than that of the blank in addition to the values of $\Delta G^{\circ}_{\text{ads}}$ which were less negative than -20 kJ mol^{-1} .
4. The adsorption of *Microdesmis puberula* root extract obeyed the Freundlich adsorption isotherm.

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