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Potential of *Microdesmis puberula* root extract as an eco-friendly inhibitor for aluminium corrosion in 2 M HCl solution

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Abstract: *The effect of Microdesmis puberula root extract on the corrosion of aluminium in 2 M HCl solution was studied using weight loss, thermometric and hydrogen evolution methods. Microdesmis puberula root extract significantly inhibited the corrosion of aluminium in HCl solution. The inhibition efficiency increased with increase in extract concentration and temperature. The experimental data conformed to the Langmuir adsorption isotherm. The spontaneity of the adsorption process was revealed by the negative values of Gibbs free energy obtained. Chemisorption process has been proposed for the adsorption of Microdesmis puberula root extract onto aluminium surface.*

Keywords: *Microdesmis puberula, Corrosion inhibition, extract, Langmuir isotherm, Chemisorption*

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I. Introduction

Corrosion results in the degradation of metals and alloys. The corrosion resistance of aluminium is very high, and is attributed to a thin oxide layer on its surface. However, this oxide layer readily dissolves in a strongly acidic or alkaline medium, with the evolution of hydrogen gas. The application of inhibitors helps in protecting aluminium in such corrosive media. In line with global best practices for a safer environment, the use of eco-friendly metal corrosion inhibitors is highly promoted. Some root extracts reported as potential inhibitors of aluminium in acidic medium include *Maesobatrya barteri* [1], ginseng [2], *Terminalia glaucescens Planch* [3] and *Capparis decidua* [4]. The need for the local sourcing of efficient eco-friendly corrosion inhibitors cannot be over-emphasised.

Microdesmis puberula plant belongs to the family Pandaceae. It is called Ntabit by the Ibibio speaking people of Nigeria. The phytochemical analysis of *Microdesmis puberula* root extract revealed the presence of cardiac glycosides, terpenes, deoxy sugars, alkaloids and saponins [5]. Spermine and spermidine derivatives are the active components isolated from *Microdesmis puberula* root exract [6]. Previous work in our group [7] revealed that *Microdesmis puberula* root extract is a good inhibitor for mild steel corrosion in acidic medium. The aim of this work is to assess the inhibitory effect of *Microdesmis puberula* root extract on the corrosion of aluminium in 2 M HCl solution.

II. Materials and Methods

2.1 Test Materials

The chemical composition of aluminium sheet used for this study was as follows (weight %): Al (99.60), Mg (0.10), Si (0.13), Mn (0.05), Fe (0.09), and Cu (0.03). 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 *Microdesmis puberula* roots were collected from a farm in Nsit Ibom Local Government Area of Akwa Ibom State, Nigeria. They were washed thoroughly with deionized water to remove dirt. The clean roots were cut into small pieces and air – dried at 30 °C for seven days and then ground to powder. The powdered root was macerated in 90% ethanol in a glass trough with cover for seven days, with intermittent stirring. The mixture was filtered. The filtrate was evaporated to constant weight in a water bath maintained at 40 °C, to obtain the crude extract.

2.3 Weight loss method

The aluminium coupons were suspended with the aid of glass hooks and rods and immersed in 100 ml of 2 M HCl solution (blank) and in 2 M HCl solution containing 1.0 g/L – 5.0 g/L *Microdesmis puberula root* extract (inhibitor) in open beakers. One aluminium coupon per beaker was used in each experiment. The beakers were placed in a thermostatic water bath maintained at 30 °C and 40 °C, respectively. The aluminium coupons were retrieved from the test solutions after 30 minutes and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing.

The inhibition efficiency I_{WL} (%), the degree of surface coverage (θ) and the corrosion rate (CR) were computed using equations (1) – (3):

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

$$\theta = \left(1 - \frac{W_1}{W_0}\right) \quad (2)$$

$$CR\,(mg\,cm^{-2}hr^{-1}) = \left(\frac{W}{A.t}\right) \quad (3)$$

where W_0 and W_1 are the weight losses of aluminium coupons in the absence and presence of extract, respectively, in 2 M HCl at the same temperature, W is the weight loss (mg), A is the total surface area (cm^2) while t is the exposure time (hours).

2.4 Thermometric Method

The instrumentation used for thermometric method of corrosion testing is as described in literature [8]. The corrodent concentration was 2 M HCl while the volume of test solution used was 50 ml. The initial temperature in all experiments was kept at 30.0 °C. The change in temperature with time was recorded using a calibrated thermometer (0 – 100 °C) to the nearest ± 0.1 °C.

The reaction number (RN) is defined as [9]:

$$RN\,(\,°C/min) = \left(\frac{T_m - T_i}{t}\right) \quad (4)$$

where T_m and T_i are the maximum and initial temperatures, respectively, while ‘t’ is the time (min) taken to reach the maximum temperature.

The inhibition efficiency, I_{TM} (%) was calculated using the formula [9]:

$$I_{TM}\,(\%) = \left(1 - \frac{RN_1}{RN_0}\right) \times 100 \quad (5)$$

where RN_0 is the reaction number in the absence of inhibitor (blank) and RN_1 is the reaction number in the presence of studied inhibitor.

2.5 Hydrogen Evolution Method

The hydrogen evolution tests (via a gasometric assembly) were carried out following standard procedure reported by other workers [10]. The reaction vessel contained 100 ml of 2 M HCl solution. One 4 cm x 5 cm aluminium coupon was dropped into the 2 M HCl solution (blank) and the reaction vessel quickly closed. The volume of H_2 gas evolved from the corrosion reaction was recorded every 60 seconds for 30 minutes. The experiment was repeated using 1.0 g/L, 3.0 g/L, and 5.0 g/L *Microdesmis puberula root* extract in 2 M HCl solution.

The inhibition efficiency I_{HE} (%) was calculated using the equation [11]:

$$I_{HE}(\%) = \left(1 - \frac{R_{H1}}{R_{H0}}\right) \times 100 \quad (6)$$

where RH_0 and RH_1 are the hydrogen evolution rates in the absence and presence of inhibitor, respectively, at a specified time.

III. Results and Discussion

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

There was a significant reduction in the corrosion rates of aluminium in 2 M HCl solution in the presence of *Microdesmis puberula* root *extract* concentration compared to the blank at 30 °C (Figure 1). A similar result was also obtained at 40 °C, though with higher corrosion rates. This reveals that the rate of corrosion of the metal was lower in the presence of the extract than in its absence. Hence, the extract inhibited the corrosion of aluminium in the HCl solution.

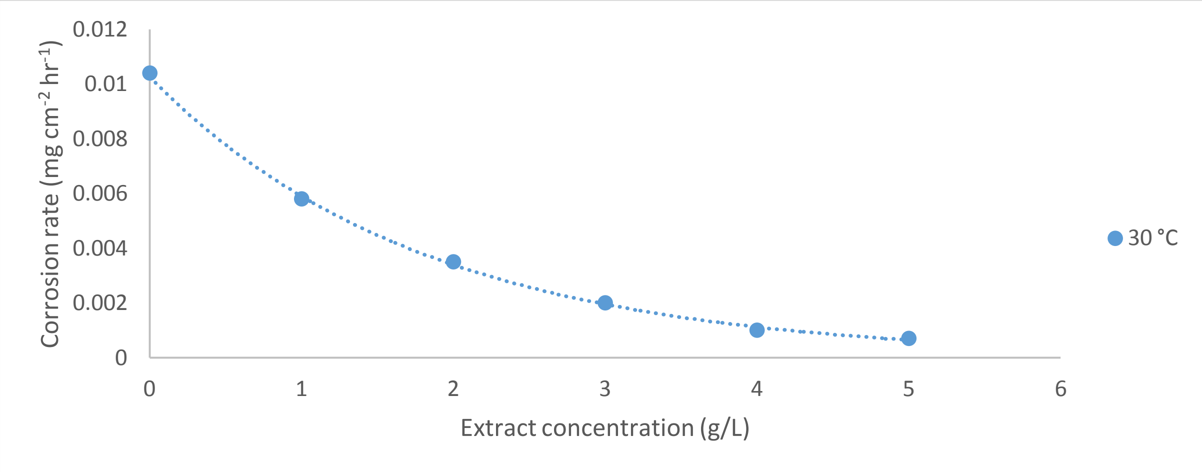

Figure 1: Variation of corrosion rate against Microdesmis *puberula root* extract concentration for aluminium in 2 M HCl at 30 °C

The inhibition efficiency by the weight loss method, at a particular temperature, increased with increase in *Microdesmis puberula* root extract concentration (Figure 2). The results of the hydrogen evolution tests, illustrated in Figure 3, indicates a marked reduction in the volume of hydrogen gas evolved in the presence of *Microdesmis puberula* root extract compared to the blank. Also, the inhibition efficiency by the hydrogen evolution method (Table 1) reveals an increase in the inhibition efficiency with increase in the root extract concentration. Additionally, the results of the thermometric tests (Figure 4) depict an increase in the time taken to reach the maximum temperature in addition to a reduction in the maximum temperature attained in the presence of the extract relative to the blank, which translates to inhibition of aluminium corrosion in the corrodent by the extract. The inhibition efficiency by the thermometric method (Table 2) also indicates an increase in the inhibition efficiency with increase in the extract concentration. The data obtained by the three methods confirm that *Microdesmis puberula* root extract inhibited the corrosion of aluminium in HCl solution.

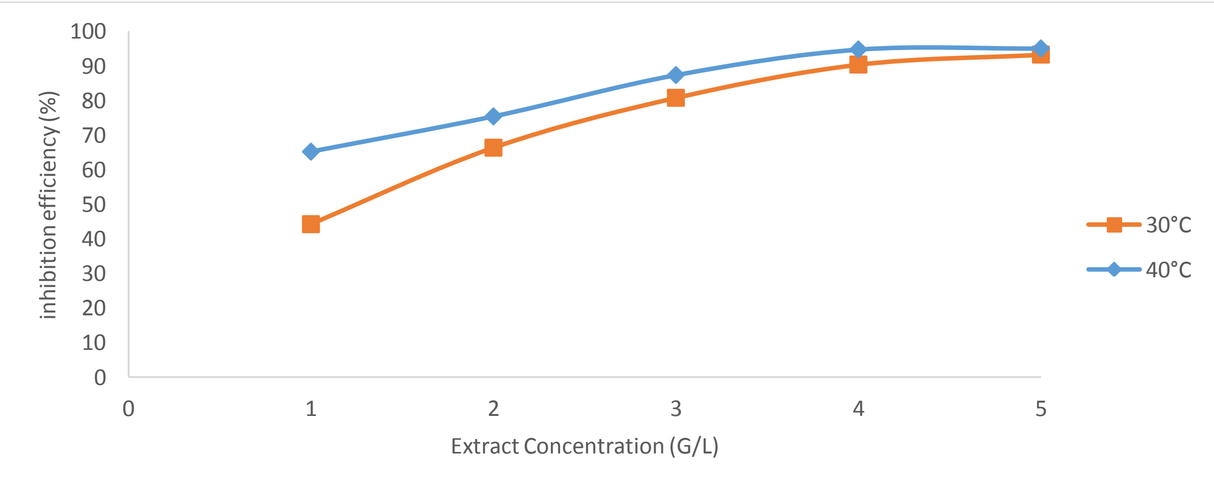

Figure 2: Effect of *Microdesmis puberula* root extract concentration on the inhibition efficiency of aluminium corrosion in 2 M HCl solution at 30 °C and 40 °C (Weight loss meaurements)

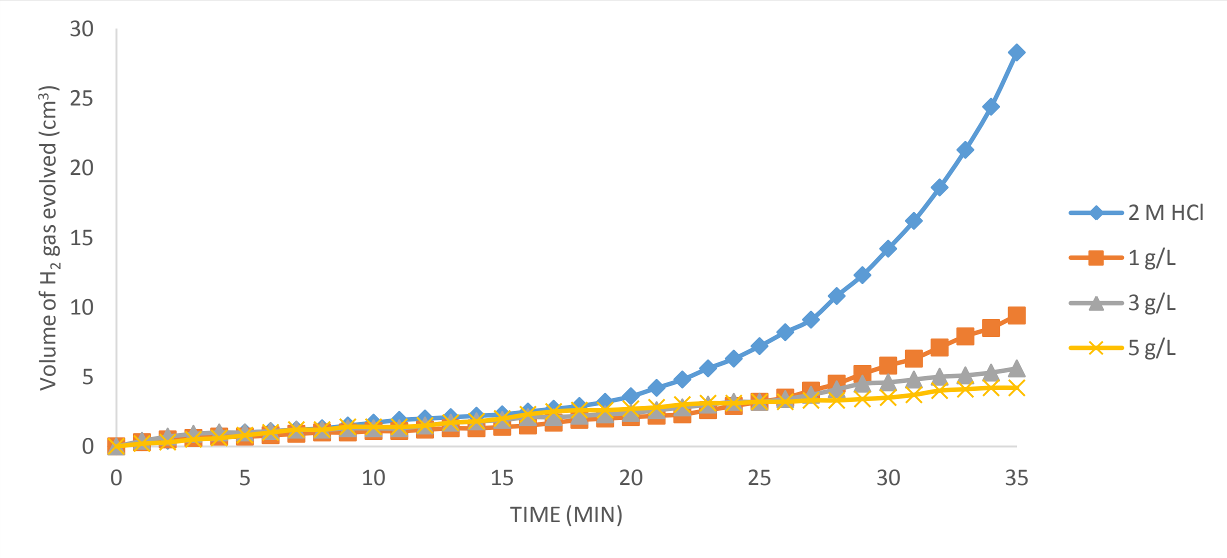

Figure 3: Variation of volume of H_2 gas evolved (cm^3) with time (min) for aluminium corrosion in 2 M HCl in the absence and presence of *Microdesmis puberula* root extract at 30 °C

Table 1: Hydrogen evolution data for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* root extract

Extract concentration (g/L)	H_2 evolution rate (cm^3 min^{-1})	Inhibition efficiency (%)
2 M HCl (Blank)	0.8086	-
1 g/L	0.2686	66.78
3 g/L	0.1600	80.21
5 g/L	0.1200	85.16

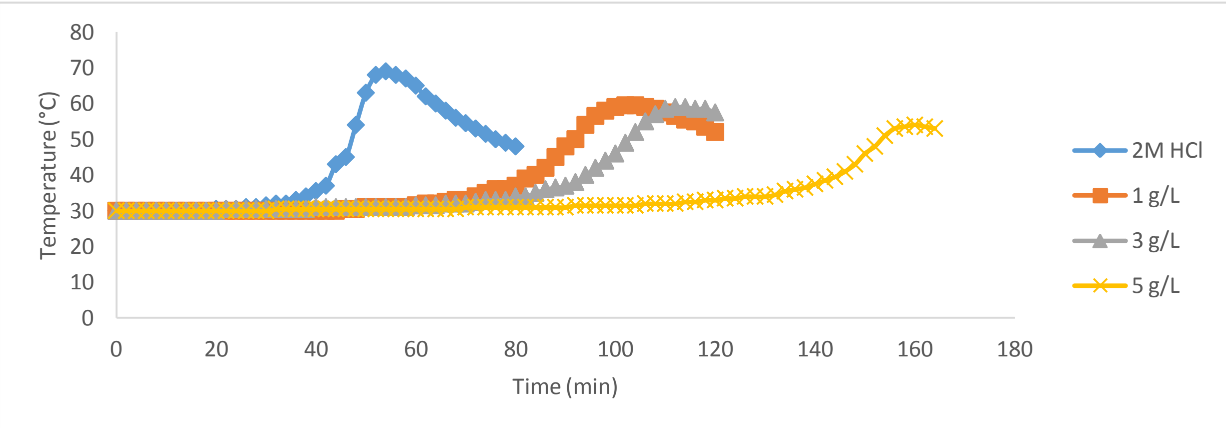

Figure 4: Variation of temperature (°C) with time (min) for aluminium corrosion in 2 M HCl in the absence and presence of *Microdesmis puberula* root extract

Table 2: Thermometric data for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* root extract

Extract Concentration (g/L)	Initial temperature T_i (°C)	Maximum temperature T_m (°C)	Time taken to reach maximum temp t (min)	Reaction number RN (°C/min)	Inhibition efficiency (%)
2 M HCl	30.0	69.0	53	0.7547	-
1 g/L	30.0	59.5	101	0.2921	61.30
3 g/L	30.0	59.0	112	0.2389	68.35
5 g/L	30.0	54.0	160	0.1500	80.12

3.2 Effect of temperature on inhibition efficiency

An increase in temperature led to an increase in the inhibition efficiency of aluminium corrosion in HCl solution by *Microdesmis puberula* root extract, by the weight loss method. The highest inhibition efficiency of 95.05% occurred at an extract concentration of 5 g/L at 40 °C. (Table 3). This indicates that the extract is more effective as an inhibitor at higher temperatures that at lower temperatures. An increase in inhibition efficiency with increase in temperature indicates a strong adsorption of the inhibitor onto the metal surface at elevated temperature as well as a chemical adsorption mechanism. Therefore, it can be proposed that the interaction between *Microdesmis puberula* root extract and aluminium surface probably occurred by a chemisorption mechanism.

Table 3: Weight loss data for aluminium corrosion in 2 M HCl solution in the absence and presence *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	30 °C	40 °C	30 °C	40 °C
2 M HCl (Blank)	0.0104	0.9201	0.520	46.005	-	-
1	0.0058	0.3202	0.290	16.010	44.23	65.20
2	0.0035	0.2263	0.175	11.315	65.77	75.40
3	0.0020	0.1163	0.100	5.815	80.77	87.36
4	0.0010	0.0483	0.050	2.415	90.38	94.75
5	0.0007	0.0455	0.035	2.275	93.27	95.05

The activation energies (E_a) of the corrosion of aluminium in HCl solution in the absence and presence of *Microdesmis puberula* root extract were calculated using the Arrhenius equation [12]:

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (7)$$

where CR_1 and CR_2 are corrosion rates at temperatures T_1 (K) and T_2 (K), respectively, while R is the universal gas constant.

The values of activation energy (E_a) obtained using equation (7) are presented in Table 4. Table 4 reveals that the E_a values in the presence of *Microdesmis puberula* root extract were lower than that of the blank (353.52 kJ mol^{-1}). The lower values of the activation energy (E_a) in the presence of the extract (inhibitor) relative to the blank coupled with an increase in the inhibition efficiency with increase in temperature could be attributed to the inhibitor being chemisorbed on the metal surface. This corroborates the view of other workers [13-14].

Table 4: Calculated values of activation energy and heat of adsorption for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* root extract

Extract concentration (g/L)	E_a (kJ/mol)	Q_{ads} (kJ/mol)
2 M HCl (Blank)	353.52	-
1	334.61	67.81
2	328.79	34.77
3	320.42	39.28
4	305.79	51.48
5	329.21	25.71

The values of heat of adsorption (Q_{ads}) were evaluated using the formula [15]:

$$Q_{ads} = 2.303\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1 T_2}{T_2 - T_1}\right] \quad (8)$$

where R is the universal gas constant while θ_1 and θ_2 are the degrees of surface coverage at T_1 (K) and T_2 (K), respectively.

The values of heat of adsorption (Q_{ads}) for the corrosion of aluminium in 2 M HCl solution are presented in Table 4. Table 4 reveals that the values of Q_{ads} obtained in this work are positive and range from 25.71 kJ mol^{-1} to 67.81 kJ mol^{-1}. Positive values of Q_{ads} signify that the adsorption of the extract onto aluminium surface and hence the inhibition efficiency increased with increase in temperature [16]. Positive Q_{ads} values are in conformity with a chemisorption process.

3.3 Adsorption isotherm

The best fit of the experimental data obtained for the adsorption of *Microdesmis puberula* root extract onto aluminium surface was found to conform to the Langmuir adsorption isotherm defined as [17]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (9)$$

where θ is the degree of surface coverage, C is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant.

Linear plot of C/θ vs. C was obtained (Figure. 5), confirming that the adsorption of *Microdesmis puberula* root extract onto aluminium surface obeyed the Langmuir adsorption isotherm. The values of K_{ads} presented in Table 5 were evaluated from the intercepts of the graph.

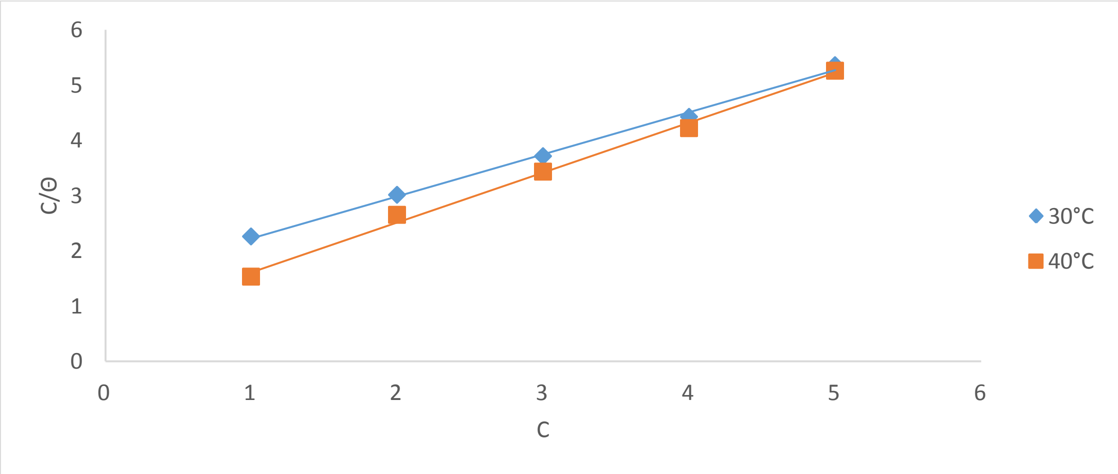

Figure 5: Langmuir isotherm plot for the adsorption of *Microdesmis puberula* root extract onto aluminium in 2 M HCl solution at 30°C and 40°C

The standard free energy of adsorption (ΔG_{ads}), was calculated using the formula [18-19]:

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5K_{ads}) \qquad (10)$$

where R is the universal gas constant, T is the absolute temperature while 55.5 is the molar concentration of water in the solution.
The values of ΔG°_{ads} obtained are also presented in Table 5. It is observed that the values of ΔG°_{ads} obtained from this work are negative. Negative values of ΔG°_{ads} indicate that the adsorption of *Microdesmis puberula* root extract onto aluminium surface occurred spontaneously. Additionally, the values of the adsorption equilibrium constant (K_{ads}) being higher at 40 °C than at 30 °C further supports the fact that the extract adsorbed more strongly onto aluminium surface as temperature increased.

Table 5: Langmuir adsorption isotherm data for aluminium corrosion in 2 M HCl solution containing *Microdesmis puberula* root extract

Temp.	R^2	n	$1/K_{ads}$ (g/ L)	K_{ads} (L g^{-1})	ΔG°_{ads} (kJ mol^{-1})
30°C	0.9969	0.76	1.4718	0.6794	-9.143
40°C	0.9955	0.90	0.7137	1.4011	-11.329

IV. Conclusion

Based on this work, the following conclusions could be made: *Microdesmis puberula* root extract has been shown to be a good inhibitor of aluminium corrosion in 2 M hydrochloric acid solution. The inhibition efficiency increases with increase in *Microdesmis puberula* root extract concentration and temperature. Chemical adsorption has been proposed to account for the adsorption of the extract onto aluminium surface, based on an increase in the inhibition efficiency with increase in temperature coupled with a decrease in the E_a value in the extract relative to the blank. The adsorption of *Microdesmis puberula* root extract onto aluminium surface has been shown to conform to the Langmuir adsorption isotherm. The negative values of ΔG°_{ads} obtained indicate that the extract adsorbs spontaneously onto aluminium surface.

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