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Aluminium Corrosion Inhibition by *Microdesmis puberula* Leaf Extract in 2 M Hydrochloric Acid Solution

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ABSTRACT
Microdesmis puberula leaf extract effectively inhibited the corrosion of aluminium in 2 M hydrochloric acid solution by both thermometric and hydrogen evolution methods. The inhibition efficiency increased with increase in *Microdesmis puberula* leaf extract concentration but decreased with increase in temperature. The inhibition efficiencies by both hydrogen evolution and thermometric methods followed the same trend. The negative values of ΔG°_{ads} obtained revealed the spontaneity of adsorption of *Microdesmis puberula* leaf extract onto aluminium surface. The adsorption of *Microdesmis puberula* leaf extract obeyed the Langmuir adsorption isotherm. Physical adsorption has been proposed for the adsorption of the extract onto aluminium surface.
Keywords: *Microdesmis puberula*, Aluminium, Corrosion inhibition, Langmuir isotherm, Physisorption, Leaf extract.

1. INTRODUCTION
The exposure of metals to corrosive media is inevitable in certain industrial processes (Abakedi et al., 2016).The use of corrosion inhibitors is very cost-effective in protecting metals in such aggressive environments. Eco-friendly inhibitors, which are extracted from natural products, are gaining prominence nowadays due to their non-toxicity, biodegradability, ease of extraction and cheapness. Plant extracts contain phytochemicals such as alkaloids, terpenes, anthraquinones, etc, which possess heteroatoms such as N, S and/or O in the combined form, through which adsorption on the metal surface are effected. Several leaves extracts (Abakedi and Asuquo, 2016a; Nathiya and Raj, 2017; Abakedi, 2017a; Ogwo et al., 2017) have been reported as good inhibitors of aluminium corrosion in acidic media. The need for the discovery of more efficient eco-friendly inhibitors for aluminium corrosion cannot be over-emphasised.
Microdesmis puberula is a valuable plant used in traditional medicare by the people of eastern Nigeria (Ajibein et al 2008; Okany et al 2012). Preliminary phytochemical screening of *Microdesmis puberula* leaf extract indicated the presence of saponins, phlobatanins, anthraquinones, cardiac glycosides, deoxy sugars, steroids, phenolic compounds and flavonoids (Henry, 2014). Previous work (Abakedi and Asuquo, 2016b) revealed that *Microdesmis puberula* leaf extract inhibited the corrosion of mild steel in acidic medium. The aim of this research was to assess the inhibition efficiency of *Microdesmis puberula* leaf extract on aluminium corrosion in hydrochloric acid solution.

2. MATERIALS AND METHODS

2.1 Test materials

The aluminium sheet used for this work had the following chemical composition (weight %): Si (0.13), Fe (0.09), Mn (0.05), Mg (0.10), Cu (0.03) and Al (99.60). The sheet was mechanically press - cut into 4 cm x 5 cm coupons. The coupons were polished to mirror surface using different grades of silicon carbide papers. The surface treatment of the coupons involved degreasing in absolute ethanol, drying in acetone and storing in a moisture – free desiccator prior to use in corrosion studies.

2.2 Preparation of *Microdesmis puberula* leaf extract

Fresh leaves of *Microdesmis puberula* were collected from a bush in Asanting Utit Ikpe, Akwa Ibom State, Nigeria. They were authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Uyo, Nigeria. They were plucked, washed and shade – dried at 30°C for seven days before grinding to powder. The *Microdesmis puberula* ethanol leaf extract was obtained as previously reported (Abakedi and Asuquo, 2016b). Extract concentrations of 0.5 g/dm^3, 1.0 g/dm^3, 1.5 g/dm^3, 2.0 g/dm^3, and 4.0 g/dm^3, respectively, in 2 M HCl solution were used for both the thermometric and hydrogen evolution tests.

2.3 Hydrogen evolution method

The instrumentation and procedure used for the hydrogen evolution (via gasometric assembly) were the same as reported by other workers (Obot et al., 2001). One aluminium coupon weighing 2.0 g was dropped into a 100 cm^3 of 2 M HCl (blank) and in 2 M HCl containing 0.5 g/dm^3 – 4.0 g/dm^3 *Microdesmis puberula* leaf extract (inhibitor), respectively, at 30°C in the reaction chamber. The volume of H_2 gas evolved from the corrosion reaction was recorded every 60 seconds for 30 minutes. The same experiments were repeated at 40°C.

The hydrogen evolution rate, R_H (cm^3 min^{-1}) was calculated using the formula (Okafor et al., 2008):

$$R_H = \frac{V_1 - V_0}{t_1 - t_0} \quad (1)$$

where V_1 and V_0 are the volumes of hydrogen gas evolved at time t_1 and t_0, respectively

The inhibition efficiency, I_{HE} (%) was calculated using the equation (Abakedi, 2017a):

$$I_{HE}(\%) = \left(\frac{R_{Hu} - R_{Hi}}{R_{Hu}}\right) \times 100 \quad (2)$$

where R_{Hu} is the hydrogen evolution rate in the uninhibited solution (blank) and R_{Hi} is the hydrogen evolution rate in the inhibited solution.

2.4 Thermometric measurements

The thermometric measurements were performed using similar equipment and procedure described by other workers (Aziz and Shams El Din, 1965). The corrodent used was 50 cm^3 of 2 M HCl. The initial temperature in all experiments was kept at 30.0°C. The progress of corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0 - 100°C) to the nearest ± 0.1°C.

The reaction number (RN) defined was obtained using the formula:

$$RN\ (°C\ min^{-1}) = \frac{T_m - T_i}{t} \quad (3)$$

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(%) was calculated using the equation:

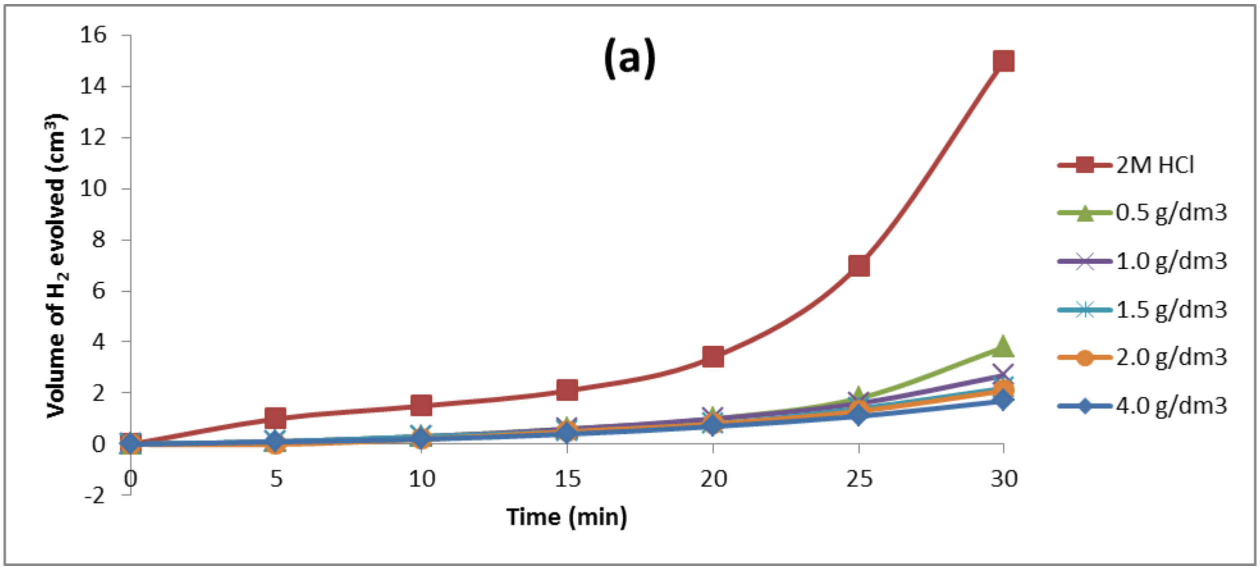
$$I_{TM}(\%) = \left(\frac{RN_0 - RN_1}{RN_0}\right) \times 100 \quad (4)$$

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.

3. RESULTS AND DISCUSSION

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

Fig. 1 reveals that the volumes of hydrogen gas evolved in the presence of various *Microdesmis puberula* leaf extract concentrations were lower than that of the blank. This implies that the extract inhibited the corrosion of aluminium in HCl solution. The inhibition efficiency by the hydrogen evolution method increased with increase in extract concentration (Fig. 2). The highest inhibition efficiency of 88.67% occurred at 30°C at 4.0 g/dm^3 *Microdesmis puberula* leaf extract concentration. Fig. 3 shows the thermometric results for the corrosion of aluminium in 2 M HCl solution (blank) and in HCl – extract medium. It is observed that an increase in extract concentration led to an increase in the time taken to reach the maximum temperature while the maximum temperature decreased. Similar results have been reported previously (Abakedi and Moses, 2016). This resulted in an increase in the inhibition efficiency with increase in *Microdesmis puberula* leaf extract concentration (Table 1). It is instructive to also note that the inhibition efficiency by both methods followed a similar trend.



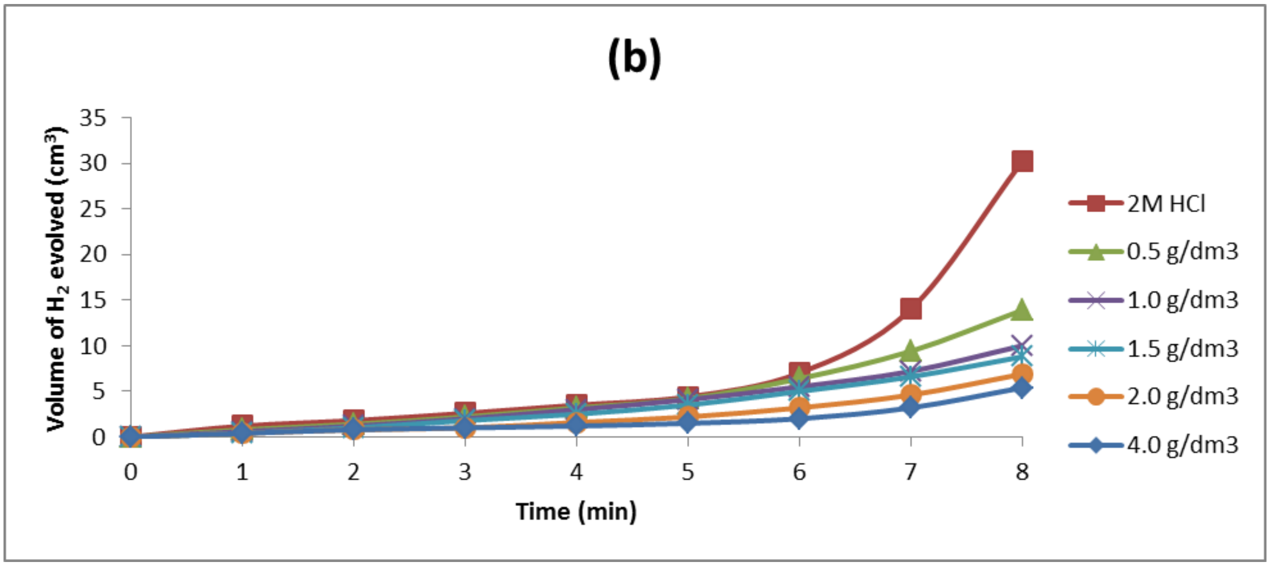


Fig. 1. Variation of volume of hydrogen gas evolved (cm^3) with time (min) for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* leaf extract concentrations at (a) 30°C and (b) 50°C

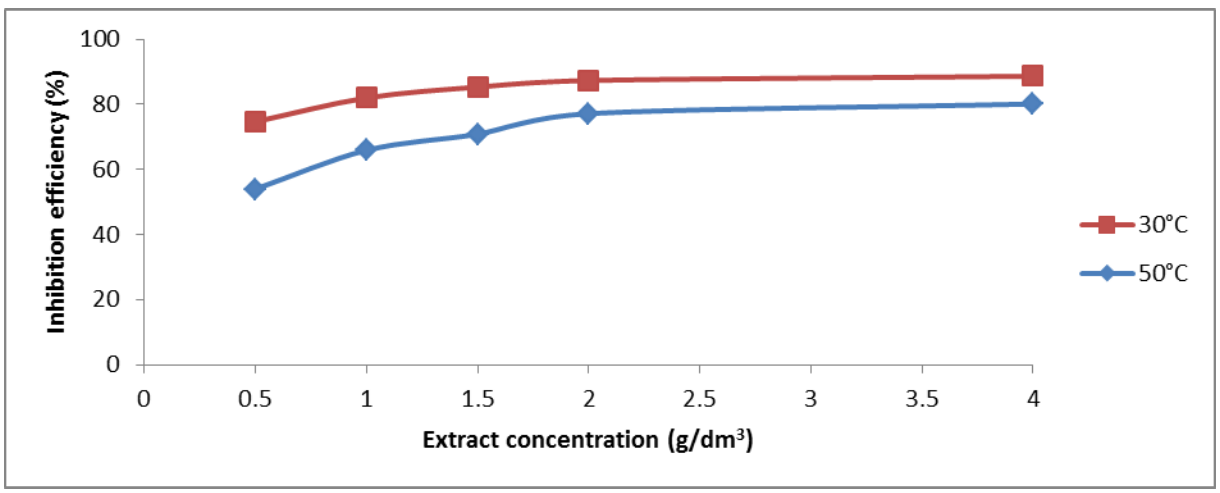


Fig. 2. Variation of inhibition efficiency (%) with *Microdesmis puberula* leaf extract concentration (g/dm^3) for aluminium corrosion in 2 M HCl solution

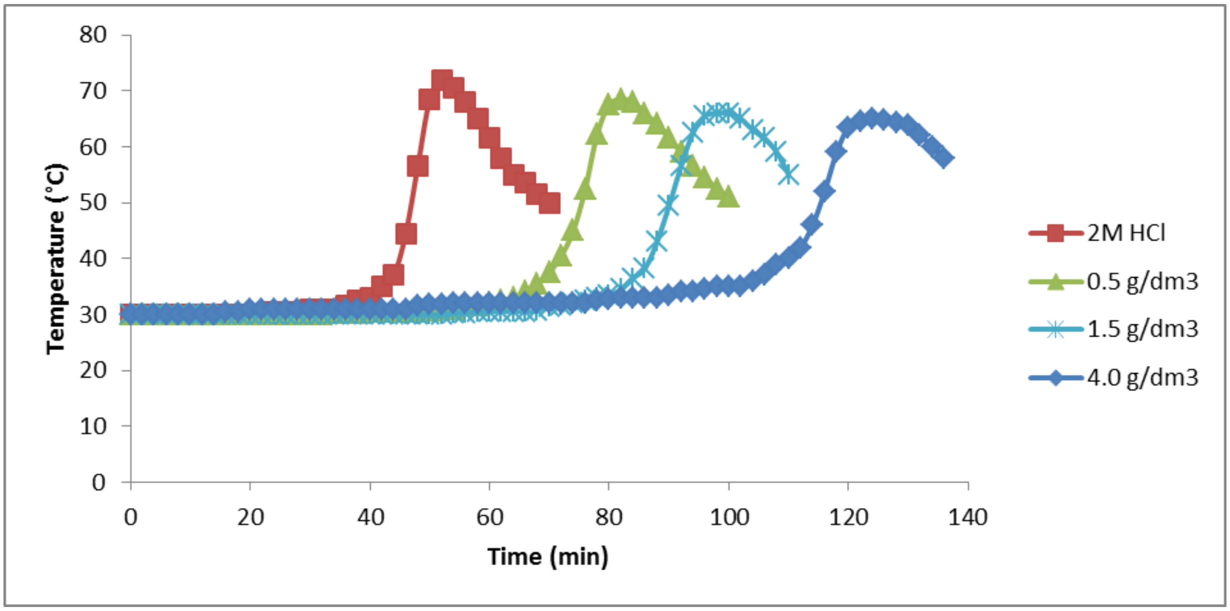


Fig. 3. Variation of temperature (°C) with time (min) for aluminium corrosion in 2 M HCl obtained in absence and presence of *Microdesmis puberula* leaf extract

Table 1. Thermometric data for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* leaf extract

Extract concentration (g/dm^3)	Initial temperature T_i (°C)	Maximum temperature T_m (°C)	Time taken to reach maximum temp. t (min)	Reaction number RN (°C min^{-1})	Inhibition efficiency (%)
Blank	30.0	72.0	52	0.8077	-
0.5	30.0	68.7	82	0.4720	41.56
1.5	30.0	66.0	99	0.3636	54.98
4.0	30.0	65.0	124	0.2823	65.05

3.2 Effect of temperature on inhibition efficiency

The inhibition efficiency of *Microdesmis puberula* leaf extract was markedly affected by temperature. Table 2 reveals that an increase in temperature resulted in a decrease in the inhibition efficiency of the extract. It has been opined that as temperature increases, the reactant molecules acquire more energy and overcome the energy barrier more easily than at lower temperatures. The increase in reaction rates due to a high temperature leads to lower inhibition efficiencies (Abakedi,2017b). Additionally, a decrease in inhibition efficiency with increase in temperature implies that the inhibitor was more effective at lower temperature than at higher temperatures and that the adsorption of the inhibitor on the metal surface occurred by a physical adsorption (physisorption) mechanism.

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

Extract concentration	Hydrogen evolution rate (cm^3 min^{-1})		Inhibition efficiency (%)	
	30°C	50°C	30°C	50°C
2 M HCl (blank)	0.5000	3.7750	-	-
0.5 g/dm^3	0.1267	1.7375	74.67	53.97
1.0 g/dm^3	0.0900	1.2875	82.00	65.89
1.5 g/dm^3	0.0733	1.1000	85.33	70.86
2.0 g/dm^3	0.0633	0.8625	87.33	77.15
4.0 g/dm^3	0.0567	0.7500	88.67	80.13

The activation energy (E_a) of the corrosion process in the absence and presence of the leaf extract was evaluated using the alternative formulation of the Arrhenius equation:

$$\log\left(\frac{R_{H2}}{R_{H1}}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

where R_{H1} and R_{H2} are hydrogen evolution rates at T_1 (303K) and T_2 (323K), respectively, and R is the universal gas constant (8.314 JK^{-1} mol^{-1}).

The values of activation energy (E_a), calculated from equation (5), are presented in Table 3. The E_a values in the presence of *Microdesmis puberula* leaf extract are higher than the E_a value for the blank (82.267 kJ mol^{-1}). Higher E_a values in the presence of inhibitor compared to the blank in addition to a decrease in the inhibition efficiency with increase in temperature indicates physical adsorption of the inhibitor onto the metal surface (Dehri and Ozcan, 2006). The adsorption of *Microdesmis puberula* leaf extract onto aluminium surface probably occurred by a physical adsorption mechanism.

Table 3. Activation energy for aluminium corrosion in 2 M HCl solution in the absence and presence of *Microdesmis puberula* leaf extract

Extract concentration	E_a (kJ mol^{-1})
2 M HCl (Blank)	82.268
0.5 g/dm^3	106.557
1.0 g/dm^3	108.281
1.5 g/dm^3	110.231
2.0 g/dm^3	106.304
4.0 g/dm^3	105.095

3.3 Adsorption isotherm

The adsorption of *Microdesmis puberula* leaf extract was found to obey the modified Langmuir adsorption isotherm defined as:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \quad (6)$$

where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium constant of the adsorption process. Plot of C/θ against C gives straight lines (Figure 4) confirming that the adsorption obeyed 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 (Ameer et al., 2000; Fouda et al., 2000):

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (7)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is the absolute temperature.

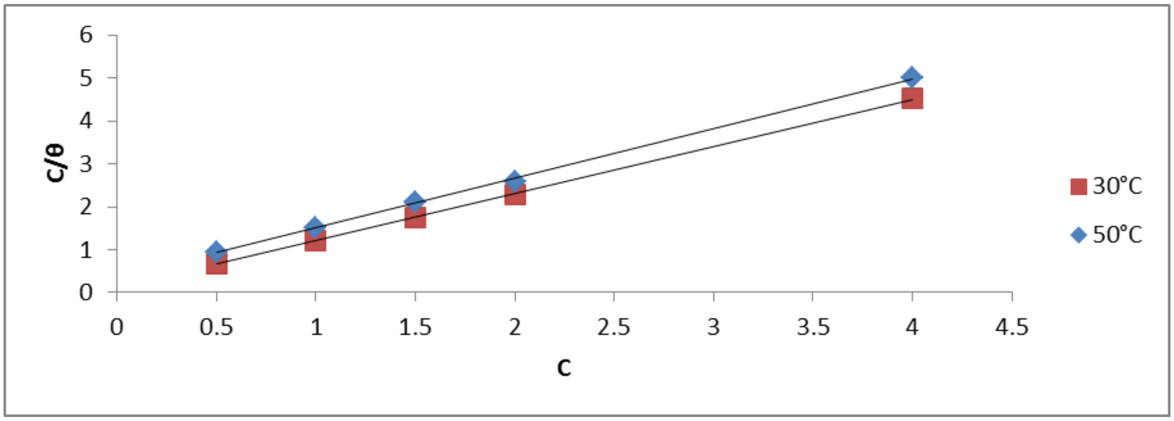


Fig. 4. Variation of C/θ vs. C (Langmuir isotherm plot) for the adsorption of *Microdesmis puberula* leaf extract onto aluminium in 2 M HCl solution at 30°C and 50°C

Table 4. Langmuir adsorption isotherm data for aluminium corrosion in 2 M HCl solution containing *Microdesmis puberula* leaf extract

Temperature	R^2	n	$1/K_{ads}$ (g dm^{-3})	K_{ads} (g^{-1} dm^3)	ΔG°_{ads} (kJ mol^{-1})
303K	0.9999	1.10	1.148×10^{-1}	8.711	- 9.747
323K	0.9993	1.16	3.462×10^{-1}	2.889	- 13.635

The negative values of ΔG°_{ads} indicate that the adsorption of *Microdesmis puberula* leaf extract onto aluminium surface occurred spontaneously. Furthermore, values of ΔG°_{ads} less negative than -20 kJ mol^{-1} are attributed to electrostatic interaction between the charged inhibitor and the charged metal surface implying a physical adsorption process. Conversely, values of ΔG°_{ads} less negative than -40 kJ mol^{-1} are generally considered to involve charge sharing between the inhibitor and the metal surface and signify a chemical adsorption process (Bilgic and Sahin, 2001; Umoren et al., 2006). The values of ΔG°_{ads} in this work being less negative than -20 kJ mol^{-1} coupled with a decrease in the inhibition efficiency with increase in temperature supports the physical adsorption of *Microdesmis puberula* leaf extract onto aluminium surface.

CONCLUSION

This research work reveals that *Microdesmis puberula* leaf extract is a good inhibitor of aluminium corrosion in HCl solution. The inhibition efficiency increased with increase in extract concentration but decreased with increase in temperature. The adsorption of *Microdesmis puberula* leaf extract onto aluminium surface best fit the modified Langmuir adsorption isotherm. The negative values of ΔG°_{ads}

reflect the spontaneity of the corrosion inhibition process. Based on a decrease in the inhibition efficiency with increase in temperature, higher E_a values in the blank than in the extract and ΔG°_{ads} values less negative than -20 kJ mol^{-1}, physical adsorption (physisorption) mechanism has been proposed for the adsorption of *Microdesmis puberula* leaf extract onto aluminium surface.

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