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Research Article

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Microdesmis puberula Stem Bark Extract as Green Inhibitor for Mild Steel Corrosion in Sulphuric Acid Solution

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Abstract The inhibitory effect of *Microdesmis puberula* stem bark extract (MPSE) on mild steel corrosion was studied using weight loss method. The rate of mild steel corrosion in MPSE-H_2SO_4 medium was greatly reduced relative to that in H_2SO_4 medium (blank). The inhibition efficiency increased with increase in the extract concentration and temperature. The highest inhibition efficiency of 82.05% was recorded at 4.0 g/L extract concentration at 60°C. The activation energies (E_a) of mild steel corrosion in MPSE - H_2SO_4 medium were lower than that in the blank. The calculated thermodynamic parameters reveal that the corrosion inhibition process was both endothermic and spontaneous. The adsorption of MPSE onto mild steel surface obeyed the Langmuir adsorption isotherm. Chemical adsorption has been proposed for the adsorption of the extract onto mild steel surface.

Keywords *Microdesmis puberula*, Corrosion inhibition, Stem bark, Langmuir isotherm, Chemisorption

1. Introduction

Corrosion inhibition studies have afforded researchers the opportunity of testing the anti-corrosion properties of materials to combat the menace of corrosion of metals in different media. Such efforts have led to the extraction of green inhibitors from natural products. Green inhibitors are assuming much prominence nowadays because they are non-toxic, cheap, renewable and environmentally friendly [1–5]. Some stem bark extracts reported as potential green inhibitors of mild steel corrosion in acidic media include *Eulychnia acida* Phil. [6], *Lannea nigritana* [7], *Maranthes polyandra* [8], [*Gmelina arborea* [9] and *Peltophorum ptetocarpum* [10]. This work is part of the global search for efficient green inhibitors of mild steel corrosion in acidic medium.

Microdesmis puberula is a medicinal plant belonging to the family Pandaceae. The stem bark extract is used in herbal medicine by the people of Gabon for the treatment of diabetes mellitus [11]. Previous studies [12] revealed that *Microdesmis puberula* root extract is a good inhibitor for mild steel corrosion in acidic medium. In furtherance of efforts geared at local sourcing of more efficient green inhibitors, the aim of this work is to assess the inhibitory effect of *Microdesmis puberula* stem bark extract on mild steel corrosion in sulphuric acid solution.

2. Materials and Method

2.1. Test Materials

The mild steel sheet used for this work had the following chemical composition (weight %): Si (0.09), Mn (0.85), C (0.12), S (0.06), P (0.05) and Fe (98.83). It was mechanically press-cut into 4 cm x 5 cm coupons. The coupons were polished to mirror finish using different grades of silicon carbide papers before degreasing in absolute ethanol, dipping in acetone and air-drying. They were then stored in a moisture-free desiccator.

2.2. Preparation of *Microdesmis puberula* stem bark extract

Microdesmis puberula stem barks were obtained from a farm in Ikot Ekpene, Akwa Ibom State, Nigeria. They were washed and air-dried under shade for seven days and ground to powder. *Microdesmis puberula* stem bark extract was obtained following standard procedures reported in literature [1,12].

2.3. Weight loss method

The cleaned and weighed mild steel coupons were suspended with glass hooks and rods and completely immersed in 100 cm^3 of 1 M H_2SO_4 solution (blank) and in 1 M H_2SO_4 solution containing 1.0 g/L – 4.0 g/L *Microdesmis puberula* stem bark extract (inhibitor) in open beakers. Each beaker contained one mild steel coupon only. The temperature of the experiment was regulated by placing the beakers in thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C, respectively. After four hours, the mild steel coupons were retrieved from the test solutions, scrubbed with bristle brush under running water, dipped in acetone and air-dried. The washed coupons were reweighed.

The corrosion rate (CR), the inhibition efficiency (I) and the degree of surface coverage (θ) were calculated using the equations below:

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

$$\mathrm{I}\ (\%) = \left(\frac{\mathrm{CR_0} - \mathrm{CR_1}}{\mathrm{CR_0}}\right) \times 100 \quad (2)$$

$$\theta = \left(\frac{\mathrm{CR_0} - \mathrm{CR_1}}{\mathrm{CR_0}}\right) \quad (3)$$

where W is the weight loss (mg), A is the total surface area of coupon (cm^2), t is the immersion time (hr), CR_0 is the corrosion rate in the absence of inhibitor while CR_1 is the corrosion rate in the presence of inhibitor.

3. Results and Discussion

3.1. Effect of *Microdesmis puberula* stem bark extract concentration on inhibition efficiency

Figure 1 reveals that there was a marked reduction in the corrosion rates of mild steel in 1 M H_2SO_4 solution in the presence of *Microdesmis puberula* stem bark extract (MPSE) concentrations compared to the blank at 30°C. Similar results were also obtained at higher temperatures, though with higher corrosion rates. The variation of inhibition efficiency with MPSE concentration for mild steel corrosion in 1 M H_2SO_4 solution is illustrated in Figure 2. It is observed that the inhibition efficiency of MPSE increased with increase in extract concentration. The highest inhibition efficiency of 82.05% occurred at 4.0 g/L MPSE concentration at 60°C. This indicates that MPSE appreciably inhibited the corrosion of mild steel in H_2SO_4 solution.

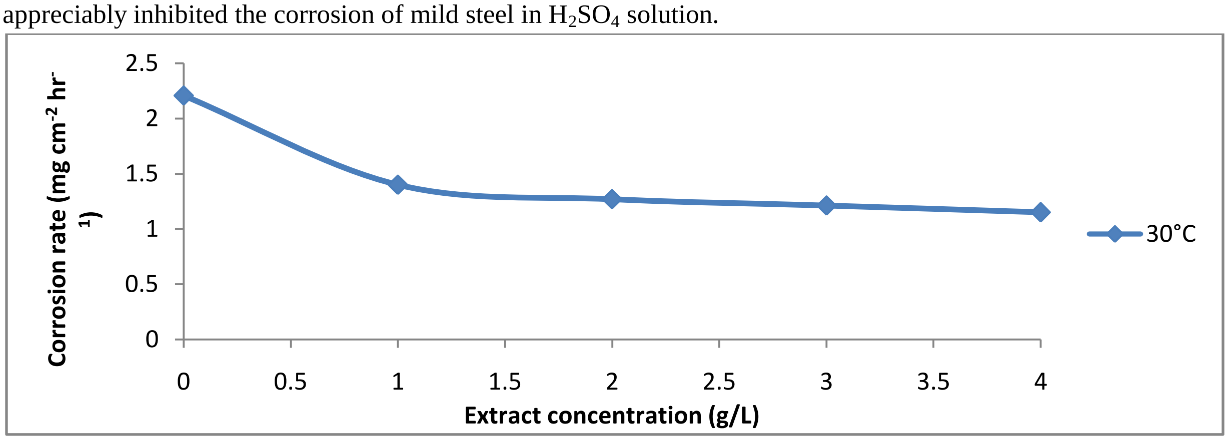

Figure 1: Variation of corrosion rate vs. Microdesmis puberula stem bark extract concentration for mild steel corrosion in 1 M H_2SO_4 solution

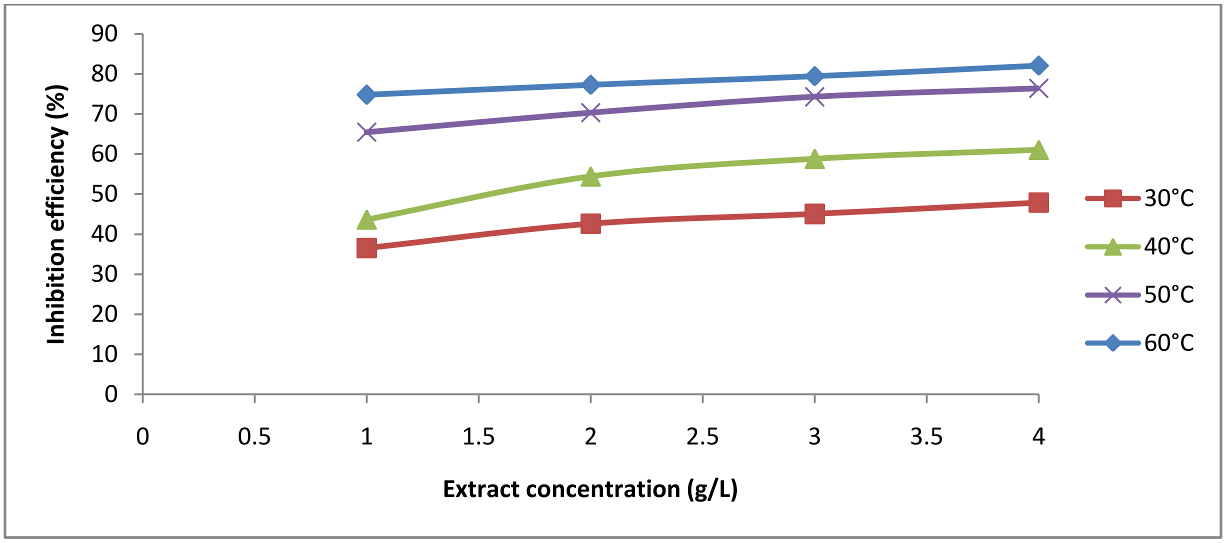

Figure 2: Effect of Microdesmis puberula stem bark extract concentration on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 solution at different temperatures

3.2. Effect of temperature on inhibition efficiency

The inhibition efficiency of *Microdesmis puberula* stem bark extract (MPSE) on mild steel corrosion in 1 M H_2SO_4 solution was affected by temperature changes. Table 1 reveals that the inhibition efficiency and surface coverage of MPSE increased with increase in temperature. This indicates that the extract was more effective as an inhibitor at higher temperatures than at lower temperatures. This is quite significant because it indicates that the extract could be used as an inhibitor in a high temperature process. Furthermore, an increase in inhibition efficiency with increase in temperature implies that the extract chemically adsorbed onto the mild steel surface.

The activation energies (E_a) of mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of MPSE , respectively, were calculated using the equation [13]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (4)$$

where CR is the corrosion rate, T is the absolute temperature, R is the universal gas constant while A is the pre-exponential factor.

The E_a values of mild steel corrosion in the absence and presence of MPSE were obtained from the gradients of ln CR vs. 1/T plots (Figure 3) and presented in Table 2. Table 2 reveals that the E_a values in the presence of MPSE were lower than the E_a value of the blank (42.440 kJ mol^{-1}). The findings in this work agree with reports in literature [14 -15] that when the E_a value in the presence of inhibitor is less than that in the blank, chemical adsorption mechanism is implied; if the E_a value in the presence of inhibitor is greater than in the blank, physical adsorption mechanism is involved. It can be proposed that MPSE chemically adsorbed onto mild steel surface.

Table 1: Weight loss data for mild steel corrosion in 1 M H_2SO_4 solution containing *Microdesmis puberula* stem bark extract

Temperature (K)	Extract concentration ($g\ L^{-1}$)	Corrosion rate ($mg\ cm^{-2}\ hr^{-1}$)	Inhibition efficiency (%)	Surface coverage
303	Blank	2.2063	-	-
	1.0	1.4000	36.54	0.37
	2.0	1.2688	42.49	0.42
	3.0	1.2125	45.04	0.45
	4.0	1.1500	47.88	0.48

313	Blank	3.1938	-	-
	1.0	1.8000	43.64	0.44
	2.0	1.4563	54.44	0.54
	3.0	1.3188	58.71	0.59
	4.0	1.2438	61.06	0.61
323	Blank	6.1688	-	-
	1.0	2.1313	64.45	0.64
	2.0	1.8313	70.31	0.70
	3.0	1.5875	74.27	0.74
	4.0	1.4563	76.39	0.76
333	Blank	9.7125	-	-
	1.0	2.4500	74.77	0.74
	2.0	2.2063	77.28	0.77
	3.0	2.0000	79.41	0.79
	4.0	1.7438	82.05	0.82

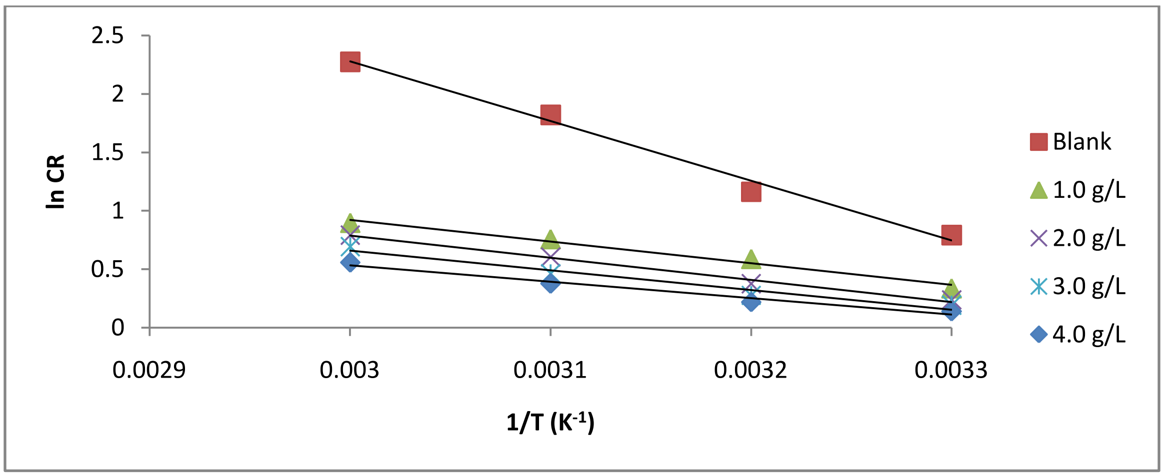

Figure 3: Variation of ln CR vs. 1/T for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of Microdesmis puberula stem bark extract

Table 2: Thermodynamic parameters for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Microdesmis puberula* stem bark extract

Extract concentration	E_a (kJ mol^{-1})	$\Delta H°_{ads}$ (kJ mol^{-1})	$\Delta S°_{ads}$ (JK^{-1} mol^{-1})
Blank	42.440	39.823	-107.432
1.0 g/L	15.362	12.746	-199.933
2.0 g/L	15.705	13.089	-200.032
3.0 g/L	14.023	11.407	-206.131
4.0 g/L	11.693	9.079	-214.160

The values of enthalpy of activation ($\Delta H°_{ads}$) and entropy of activation ($\Delta S°_{ads}$) were evaluated from the transition state equation [16]:

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\circ}_{ads}}{R}\right] - \frac{\Delta H^{\circ}_{ads}}{RT} \quad (5)$$

where CR is the corrosion rate, R is the universal gas constant, T is the absolute temperature, N is Avogadro's number, A is the Arrhenius pre-exponential factor and h is the Planck's constant. Figure 4 reveals linear plots of ln (CR/T) vs. 1/T for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of MPSE. The values of ΔH^o_{ads} were evaluated from the gradients while the values of ΔS°_{ads} were obtained from the intercepts of the plots and are presented in Table 3. Positive values of ΔH^o_{ads} obtained both in the blank and in the presence of the extracts imply that the mild steel corrosion process was endothermic. The values of ΔS^o_{ads}, being negative, indicate a decrease in disorderliness during the adsorption of MPSE onto mild steel surface.

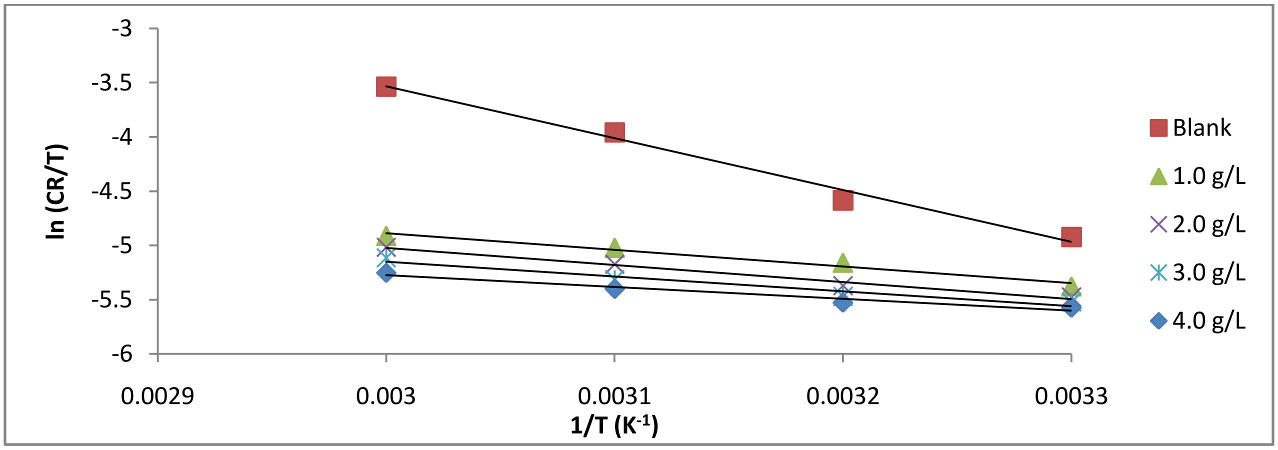

Figure 4: Variation of ln (CR/T) vs. 1/T for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of Microdesmis puberula stem bark extract

3.3. Adsorption Studies

The type of interaction between the metal surface and the inhibitor can be deduced by the adsorption isotherm obeyed by the adsorption process. Of the several adsorption isotherms tested, the adsorption of MPSE on mild steel surface conformed to the modified Langmuir adsorption isotherm defined as:

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

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

Linear plots of C/θ vs. C (Figure 5) signify that the adsorption of the extract conformed to the Langmuir adsorption isotherm. The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 3. It is observed that the values of K_{ads} increased with increase in temperature. An increase in the values of K_{ads} with increase in temperature indicates that the extract become more strongly adsorbed onto mild steel surface as temperature increases [17].

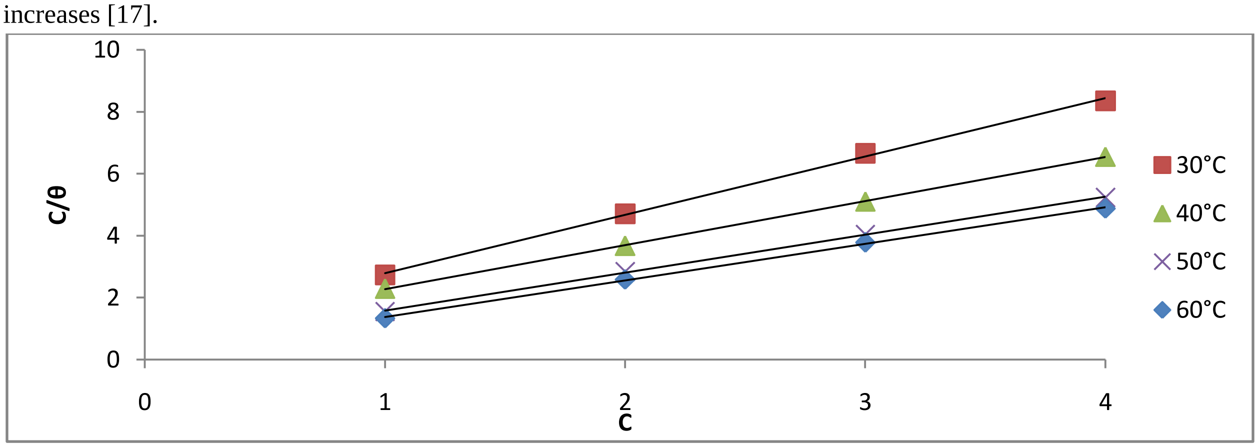

Figure 5: Langmuir isotherm plot for mild steel corrosion in 1 M H_2SO_4 solution containing Microdesmis puberula stem bark extract at different temperatures

Table 3: Langmuir isotherm parameters for the adsorption of *Microdesmis puberula* stem bark extract on mild steel surface in 1 M H_2SO_4 solution

Temperature (K)	**R^2**	**n**	**$1/K_{ads}$ (g L^{-1})**	**K_{ads} (g^{-1} L)**	**$\Delta G°_{ads}$ (kJ mol^{-1})**
303	0.9998	1.88	0.9131	1.0952	-10.347
313	0.9999	1.42	0.8542	1.1707	-10.862
323	0.9996	1.22	0.3557	2.8114	-13.562
333	0.9991	1.18	0.1938	5.1600	-15.663

The standard energy of adsorption ($\Delta G°_{ads}$) also presented in Table 3 was calculated using the equation [18]:

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

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 negative values of $\Delta G°_{ads}$ indicate the spontaneity of adsorption of MPSE onto mild steel surface.

4. Conclusion

Based on this work, the following conclusions are made:

- *Microdesmis puberula* stem bark extract inhibited the corrosion mild steel in 1 M H_2SO_4 solution compared to the blank.
- The inhibition efficiency of *Microdesmis puberula* stem bark extract increased with increase in extract concentration and temperature.
- The adsorption of *Microdesmis puberula* stem bark extract on mild steel surface obeyed the Langmuir adsorption isotherm.
- Based on an increase in inhibition efficiency with increase in temperature coupled with the E_a values in the presence of MPSE being lower than that of the blank, chemical adsorption (chemisorption) of *Microdesmis puberula* stem bark extract onto mild steel surface has been proposed.

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