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Thermodynamic, Kinetic and Adsorptive Parameters of Corrosion Inhibition of Mild Steel Using Polyalthialongifolia Bark Extract in 0.5M H_2SO_4

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Abstract:

The inhibitive action of Polyalthialongifolia bark extracts on the corrosion of mild steel in 0.5 M H_2SO_4 has been studied using the weight loss technique. The concentration of the extract used was varied (0.1, 0.2, 0.3, 0.4, and 0.5) g/l over an exposure period of 24 hours and the temperature variation was 303 k, 323 k and 343 k respectively. The corrosion rates decreased generally with increase in inhibitor concentration. The inhibition efficiency was found to increase with increasing inhibitor concentration. The effect of temperature on the corrosion inhibition of the mild steel indicated an increase in the corrosion rate as temperature increased and subsequent decrease in the inhibition efficiency. Thermodynamic data calculated are suggestive of adsorption of inhibitor molecules on metal surface. Experimental data fitted into Langmuir's and Temkin's adsorption isotherms.

Keywords: Mild steel, Polyalthialongifolia bark, Weight loss method, Adsorption, Kinetic

1. INTRODUCTION

Polyalthialongifolia (masquerade tree) is an evergreen plant commonly used as an ornamental street tree due to its effectiveness in combating noise pollution. Polyalthialongifolia is also known as false Ashoka, Buddha Tree, Green champa, Indian mast tree, and Indian Fire tree. It exhibit symmetrical pyramidal growth with willowy weeping pendulous branches and long narrow lanceolate leaves with undulate margins. The tree is known to grow over 30 ft in height (Evergreen tree can grow up to a height of 15-20 meters tall [1]. It contains several organic compounds of high molecular weight with heteroatoms such as tannins, saponins, alkaloids, and phenols which are capable of adsorbing onto the metal surface. The use of synthetic compounds as corrosion inhibitors are desirable due to their metal protecting properties, however, the problem of toxicity, non-degradability and environmental pollution posed by these compounds have been of serious concern [2]. Corrosion is the deterioration of materials by chemical interaction with their environment. The consequences of corrosion are many and its effects on the safe, reliable and efficient operation of equipment or structures are severe. Throughout the ages, plants have been used by human beings for their basic needs such as shelters, production of food stuffs, fertilizers, flavors and fragrance, clothing, medicines and last but not the least, as corrosion inhibitors as noted by [3]. The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Corrosion inhibitors are chemicals either synthetic or natural which when added in small quantity to an environment decrease the rate of attack by the environment on metals [4].

2. METHODS

2.1 Materials

Mild steel of known composition as presented in Table 1 obtained from Universal steel company Lagos, Nigeria was used for this work.

Table 1: Chemical Composition of the Mild Steel used

Element	Fe	C	Si	Mn	S	P	Cr	Ni	Cu	Al	Mo	V	Ti
Composition(%)	97.75	0.21	0.25	0.77	0.03	0.02	0.13	0.13	0.33	0.29	0.02	0.003	0.009

2.2 Inhibitor Preparation

Polyalthialongifolia barks were collected from Nsukka Local Government Area in Enugu State, Nigeria. Fresh bark were cut in to small pieces and shade dried. It was later pound to powder using mortar. The extract was prepared by refluxing 10 g of the powder in 500 ml of methanol for 5 days. The extract was filtered and various concentrations 0.1, 0.2, 0.3, 0.4 and 0.5 g/l was prepared [5].

2.3 Phytochemical examination

The phytochemical screening of Polyalthialongifolia barks extract was carried out using standard procedure [6, 7].

2.4 Weight loss measurements

The samples were completely weighed before immersed in 250 ml of the test solution with and without the addition of different concentrations of Polyalthialongifolia extracts. The beaker was inserted into a water bath maintained at a temperature of 303k, 323k and 343k over an exposure time of 24h respectively. Each sample was withdrawn from the test solution, washed with water and rinsed with acetone and air dried before re-weighing. This procedure was repeated for the varied temperatures. The difference in weight was recorded as the weight loss. From the weight loss, the corrosion rates (CR) were calculated using the equation

$$\mathbf{CR} = \frac{87.6W}{DAT} \ \mathbf{mm/yr} \qquad \mathbf{(1)}$$

Where W= weight loss in mg

D= density g/cm3

A= area in cm2

T= exposure time in hours

From the corrosion rate, the inhibition efficiency, (IE %) was calculated using the equation

$$\mathbf{IE\%} = \frac{CRo - CR}{CRo} \ \mathbf{x\ 100} \qquad \mathbf{(2)}$$

Where CRo is the corrosion rate without inhibitor and CR is the corrosion rate in the presence of inhibitor. The surface coverage, ϴ, was calculated from the corrosion rate as follows:

$$\mathbf{\Theta} = \frac{CRo - CR}{CRo} \qquad \mathbf{(3)}$$

3. RESULTS AND DISCUSSION

3.1 Phytochemical screening of Polyalthialongifolia

Table 1 shows the phytochemical screening of methanol extract of Polyalthialongifolia bark. The results obtained indicate that Tannins, Saponins, Flavonoids, steroids, Phenols and Alkaloids are present in the methanol extract of Polyalthialongifolia bark extracts, hence the inhibition efficiency of methanol extract of plant may be attributed to the phytochemical constituent of the extract

Table 2: Qualitative phytochemical analysis of Polyalthialongifolia (Methanol)

Compound	Bark
Alkaloid	+
Phenol	+
Tannins	+
Saponins	+
Flavonoids	+
Steroids	+
Reducing Sugar	+

3.2 Effect of inhibitor concentration on corrosion rate

The variation of corrosion rate with immersion time at different temperatures is shown in Figure 1 and it was observed that the corrosion rate of the mild steel decreased with addition of inhibitor. At 303 k, the corrosion rate for the control is 62.91 mm/yr but this value was reduced to 7.82 mm/yr in the presence of inhibitor. Similar trend was observed with various temperatures studied. This may be due to the increased protection offered by the inhibitor as concentration increases, thereby preventing the breakdown of the passive films leading to an increase in the corrosion resistance of the mild steel compared with the uninhibited samples [7]. The least corrosion rate was obtained at 303 k and with 0.5 g/l concentration. However, as the temperature increased, the corrosion rate increase with the temperature of 343 k having the highest values of corrosion rates. This could be that there is desorption of inhibitor from the surface of the mild steel or break down of protective film formed earlier due to increase in temperature thereby exposing it to the aggressive environment.

3.3 Effect of inhibitor concentration on inhibitor efficiency

In Figure 2 the variation of inhibitor efficiency with inhibitor concentration is shown. The inhibition efficiency increased with increase in the concentration of Polyalthialongifolia bark extract. At a temperature of 303 k, maximum inhibition efficiency of 87.57 % was obtained at 0.5 g/l inhibitor concentration. The reduction in inhibition efficiency at 323 k and 343 k can be attributed to the acceleration of the breakdown of the passive film at higher temperature.

3.4 Effect of Temperature

The effect of temperature on the corrosion of mild steel in the absence and presence of Polyalthialongifolia bark was studied using the Arrhenius state equation as shown in Equations (4) and (5) [8].

$$\log CR = \log A - Ea/2.303RT \qquad (4)$$

$$\log\left(\frac{CR}{T}\right) = \{\log(R/NA\,h) + \Delta Sa/2.303R\} - \Delta Ha/2.303RT \qquad (5)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, $E_{a.}$ is the activation energy, R is the universal gas constant and T is the temperature of the system. N_A is the Avogadro's constant, ΔSa is the entropy of activation and ΔHa is the enthalpy of activation. From Equation 4, plot of log CR versus reciprocal of absolute temperature, 1/T is as presented in Figure 3, which gives a straight line with slope equal to $-\frac{Ea}{2.303R}$, from which the activation energy for the corrosion process can be calculated.

From Equation (5), plot of $Log\ CR/T$ versus reciprocal of absolute temperature, $1/T$, as shown in Figure 4 gives a straight line with slope equal to - $\frac{\Delta Ha}{2.303R}$ and intercept of $\left[Log\frac{R}{NAh} + \frac{\Delta Sa}{2.303R}\right]$, from which the enthyalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 3. The values of the extrapolated activation energy, Ea were found to be greater where corrosion rate were inhibited than those obtained where there were no inhibition indicating that the extracts of *Polyalthialongifolia* bark retarded the corrosion of the alloy in the studied medium. It was also found that the activation energy was lowered than the value of 80 kJ/mol. required for chemical adsorption to take place, confirming that the adsorption occur through the mechanism of physical adsorption [9]. The increase in the activation energy is achieved presumably via formation of a thin coat or film on the metal surface that has become a barrier to both energy and mass transfer. However, increasing the solution temperature weakens the inhibition effect by enhancing the counter process of desorption. That is why the inhibition efficiency values decreased with increase in temperature.

3.5 ADSORPTION ISOTHERM

The adsorption behavior of Polyalthialongifolia bark extract was investigated. The test revealed that adsorption of bark extract on the surface of the mild steel is constant with Langmuir and Temkin adsorption isotherms. Langmuir adsorption model can be represented as follows

$$\frac{c}{\theta} = \frac{1}{K} + c \qquad (4)$$

Where c is the inhibitor concentration and K is the adsorption equilibrium constant representing the degree of adsorption? Θ is the degree of surface coverage [10]. Taking the

$$log\frac{c}{\theta} = c + 1/k \qquad (5)$$

Logarithm of equation 4, equation 5 is obtained. The plot of log c / Θ versus log c as shown in Figure 5 gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of *Polyalthialongifolia* bark on the surface of the mild steel.

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy ($\Delta G^o{}_{ads}$) was obtained according to [10].

$$\Delta \mathbf{Gads} = -\mathbf{RT}\ \ln(\mathbf{55.5\ K}) \qquad \textbf{(6)}$$

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water and

$K_{ads} = \Theta/(1 - \Theta)\ C$.

Calculated values of the free energies are presented in Tables 4 and 5. Generally, values of $\Delta G^o{}_{ads}$ around -20 kJ / mol or lower are consistent with the electrostatic interaction between the charge molecules and the charged metal (physisorption); those around -40 kJ / mol or higher involve charge sharing or charge transfer from organic molecule to the metal surface to form a coordinate type of bond (chemisorptions) [11]. From the result obtained, the values were found to be negative, physisorption, and a suggestion that the adsorption of *Polyalthialongifolia* bark onto the mild steel surface is a spontaneous process and adsorbed layer is stable [12].

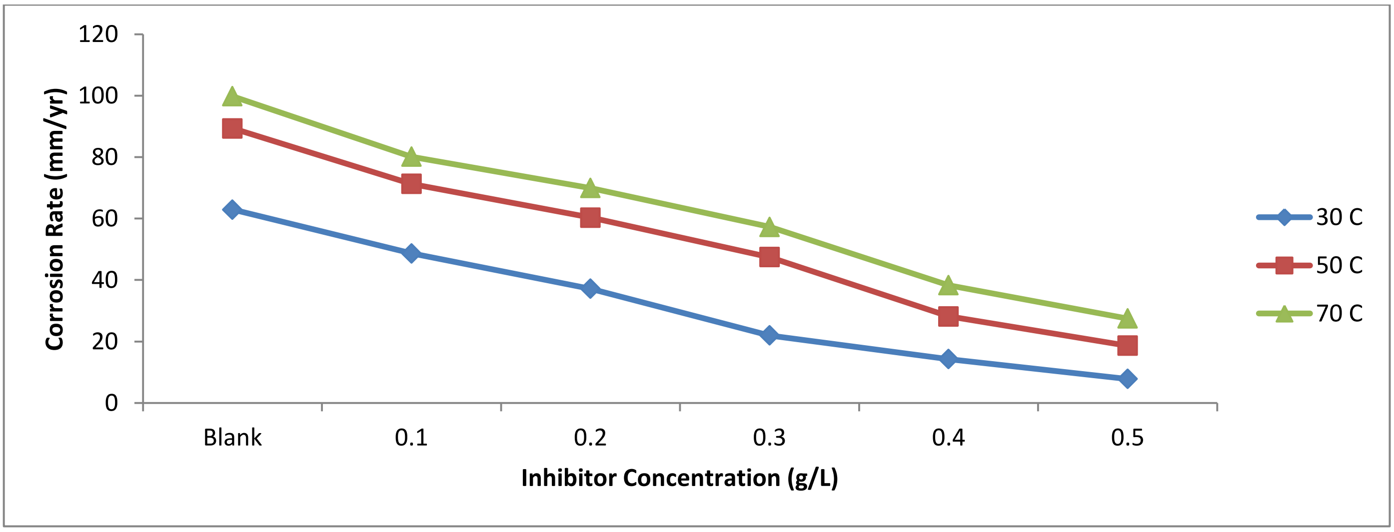

Figure 1: Variation of Corrosion Rate against Inhibitor Concentration of Mild Steel in the Absence and Presence of Polyalthialongifolia Bark Extract

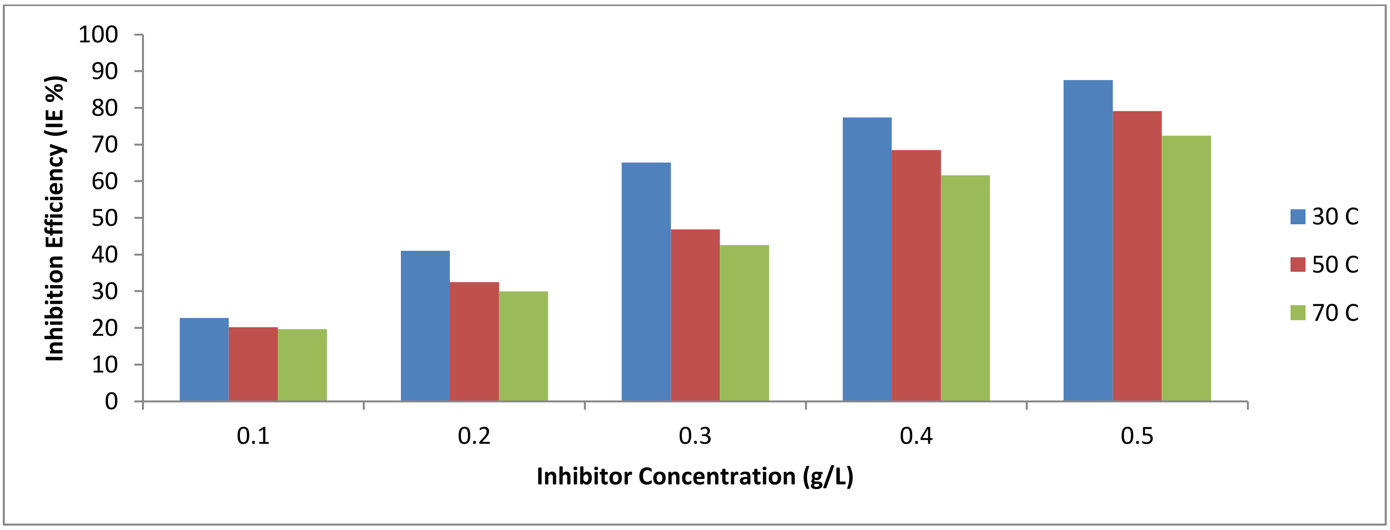

Figure 2: Variation of Inhibition Efficiency Against Inhibitor Concentration of Mild Steel in the Absence and Presence of Polyalthialongifolia Bark Extract

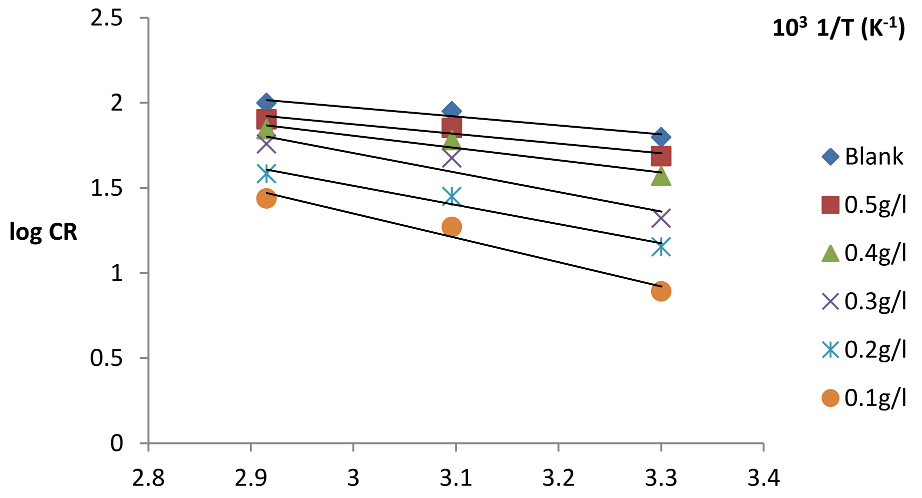

Figure 3: Variation of log CR with 1/T of mild steel in 0.5 M H2SO4 in the Absence and Presence of Polyalthialongifolia Bark Extract

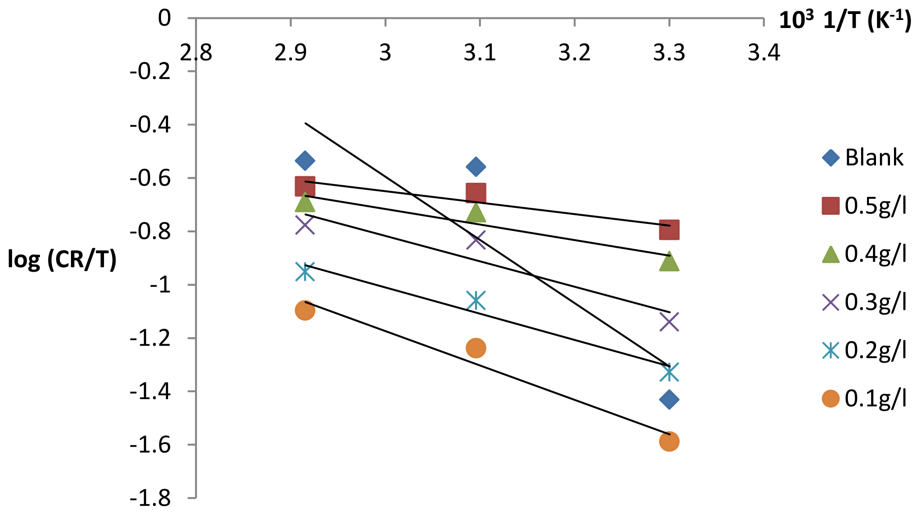

Figure 4: Variation of log (CR/T) versus 1/T of mild steel in 0.5 M H2SO4 in the Absence and Presence of Polyalthialongifolia Bark Extract

Table 3: Activation parameters E_a, ΔH_a, ΔS_a, and Q_{ads} for mild steel in 0.5 M H_2SO_4 in the Absence and Presence of Polyalthialongifolia Bark Extract

Inhibitor Concentration (g/L)	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (kJ/mol)	Q_{ads}(kJ/mol)
Blank	10.05	45.36	- 72.95	-
0.1	27.34	24.64	- 146.19	- 3.92
0.2	21.50	18.84	- 160.50	- 10.52
0.3	21.96	18.25	- 158.54	- 19.91
0.4	13.81	11.14	- 178.05	- 16.32
0.5	10.89	8.21	- 185.50	- 21.52

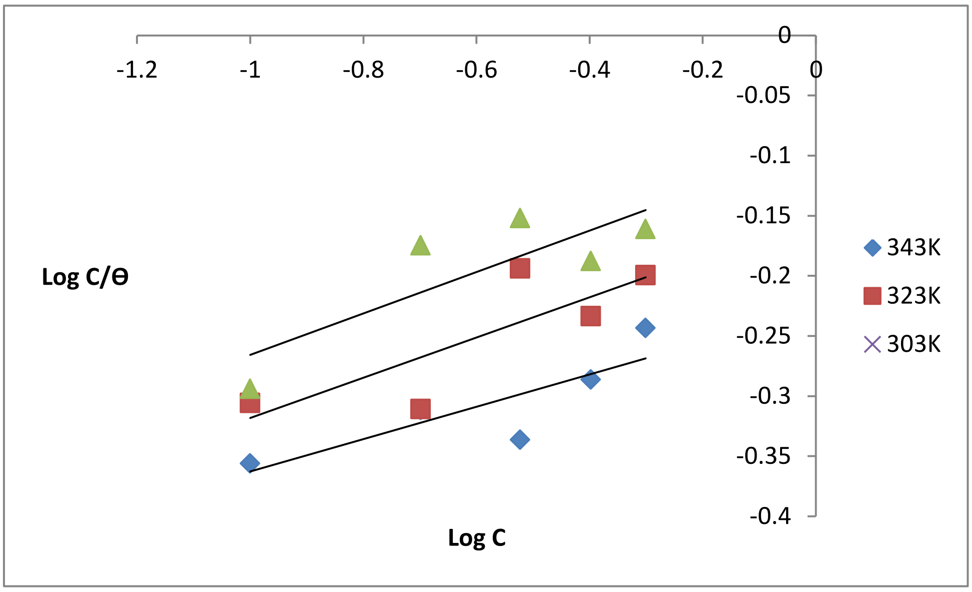

Figure 5: Langmuir Isotherm for the Adsorption of the Inhibitor on Mild Steel Surface in 0.5 M H2SO4 Solution at Various Temperatures

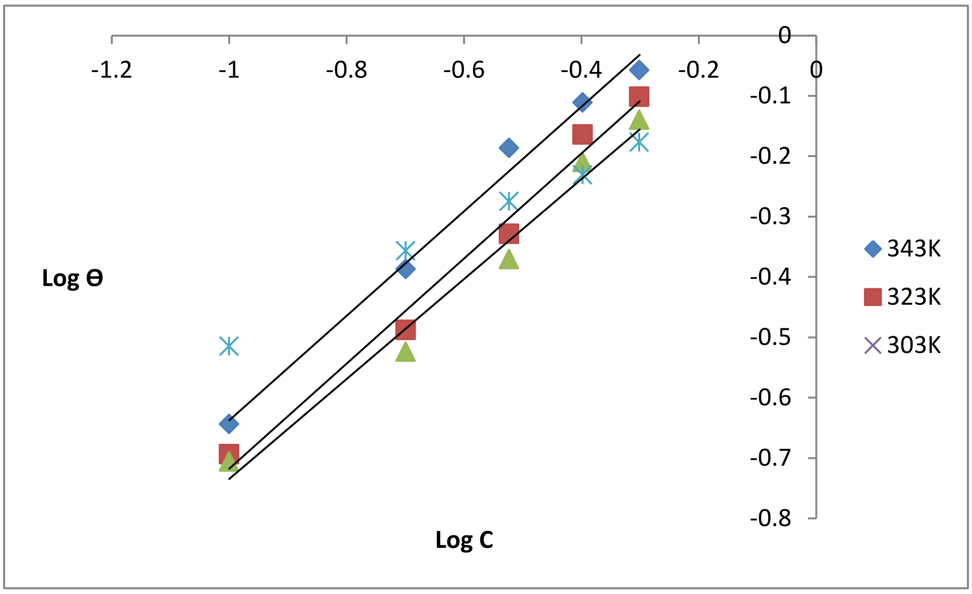

Figure 6: Temkin Isotherm for the Adsorption of the Inhibitor on Mild Steel Surface in 0.5 M H2SO4 Solution at Various Temperatures

Table 4: Temkin Plots values for calculating free energy (ΔG)

Temperature (K)	R^2	Slope	Intercept	(ΔG)(kJ/mol)
303k	0.980	0.827	0.093	4.14
323k	0.986	0.870	0.152	5.73
343k	0.990	0.865	0.228	7.24

Table 5: Langmuir Plots values for calculating free energy (ΔG)

Temperature (K)	R^2	Slope	Intercept	(ΔG)(kJ/mol)
303k	0.681	0.172	- 0.093	4.14
323k	0.667	0.167	- 0.150	5.69
343k	0.710	0.134	- 0.228	7.24

4. CONCLUSIONS

From the results of weight loss of corrosion rate of mild steel using Polyalthialongifolia bark extract as corrosion inhibitor, the following conclusions were drawn:

1 The corrosion rate in the presence of Polyalthialongifolia bark (inhibitor) decreases with increase in the concentration of the inhibitor
2 The extract Polyalthialongifolia bark can be used as inhibitor for mild steel in the medium.
3 The percentage inhibition efficiency (% IE) increased with increase in concentration of the inhibitor. However, it decreases with increase in temperature.
4 It has been established that the adsorption process followed a physisorption.

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CONFLICT OF INTEREST

There is no conflict of interest associated with this work

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