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# *COSTUS AFER* LEAVE EXTRACT AS NONTOXIC CORROSION INHIBITOR FOR MILD STEEL IN $H_2SO_4$

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## ABSTRACT

The corrosion inhibition performance of the ethanol extracts of *Costus afer* leaves (EECAL) on the corrosion of mild steel in 5 M $H_2SO_4$ solutions at 303K and elevated temperatures of 313, 323 and 333 K was investigated using weight loss method (gravimetric) and hydrogen evolution (gasometric) techniques respectively. The results indicate that the leave extract inhibit the corrosion of mild steel with maximum inhibition efficiency (93.1%) at 3.0g/L. Generally the inhibition efficiency was found to increase with increase in concentration of the leave extract but decreased with rise in temperature. Inhibition mechanism was deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of the leave extract on the mild steel coupon was found to obey the Langmuir, Temkin, Frumkin and Freundlich adsorption isotherms.

**KEYWORDS**: Mild steel, *Costus afer*, Adsorption isotherm, Physical adsorption

## 1.0. INTRODUCTION

Metallic materials are still the most widely used group of materials particularly in both mechanical engineering and the transportation industry. In addition, metals are commonly used in electronics and increasingly also in the construction industry. There are several ways of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials (Saratha and Meenaushi, 2010). The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one among the acceptable practices used to reduce and/or prevent corrosion. Large number of organic compounds have been studied and analyzed to investigate their potential as corrosion inhibitors. Most of this studies revealed that almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorus and oxygen show significant inhibition efficiency (Singh and Anaya 2007; Benali *et al*, 2013). Despite these promising findings about possible corrosion inhibitors, most of these substances are not only expensive but also toxic and non-biodegradable, thus causing pollution problem. Hence these deficiencies have prompted the search for their replacement. Furthermore, the use of naturally occurring compounds are of interest, because of their cost effectiveness, abundant availability, and more importantly their environmentally acceptability (El-Etre *et al*, 2005). Due to these advantages, extracts of some common plants and plant products have been tried as corrosion inhibitors for metals and alloys under different environment. The above attributes have made plants become an important source of a wide range of eco-friendly (green) corrosion inhibitors (Saratha *et al*, 2009).

*Costus afer* is a member of the family Costaceae and specie of the genus Costus. It is known by the common name Bush cane or Ginger lily. The plant is mostly found in swampy areas. The succulent part of the stem is edible while leaves are used to feed animals. *Costus afer* leave has been remedies of many diseases.

This present work is aimed at investigating the effect of different concentrations of extracts of *Costus afer* leaves on the corrosion of mild steel in HCl solution using gravimetric and gasometric techniques. Use of inhibitors is an important task in the protection of metals from corrosion. Till now the majority of metal corrosion inhibitors used is toxic for humans and the environment. The choice of the present inhibitors is based on the following considerations: Investigation of *Costus afer* Leaves Extract shows that it is:

- Less-expensive
- Non toxic
- Possess no threat to the environment
- Easily available

## 2.0. Experimental Procedures

### 2.1. Material collection and preparation

The sheet of Mild Steel used for this study has the following composition: Fe (98.34%) C (0.19%), Si

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(0.26%), Na (0.64%), S (0.05%), P (0.06%), Ni (0.09%), Cr (0.08%), Mo (0.02%), and Cu (0.27%). This was obtained from Ejison Nig. Ltd, Calabar, Cross River State – Nigeria. The sheet was mechanically press-cut into 4.00 x 0.08 x 5.00cm coupons for the weight loss experiment and 4.00 x 0.08 x1.80 cm for hydrogen evolution. These were polished with different grades of emery paper, degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator prior to use. The aggressive acidic solution of 5 M $H_2SO_4$ was prepared by dilution of analytical grade $H_2SO_4$ with distilled water and all experiments were carried out in unstirred solutions and all weighing were done with AE ADAM digital analytical balance. Distilled water was used to prepare all experimental solutions.

### 2.2. Preparation of *Costus afer* leaves

The required leaves – *Costus afer* leaves were collected from a local bush in Nigeria. These leaves were dried in a laboratory oven at 60°C, and ground into powder form. The powdered sample was extracted continually with absolute ethanol in a Soxhlet Extractor for 24 hours. The extract obtained was later heated on heat stirrer machine at a temperature of 60°C until most of the ethanol evaporated. 5g of the ethanol extract of the plant was diluted with appropriate volume of the $H_2SO_4$ acid solutions then kept for 24 hours, filtered and stored. From the stock solution (5 g/L), inhibition test solutions were prepared to obtain 0.1 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L and 3.0 g/L for weight loss and hydrogen evolution measurements, respectively.

### 2.3. Weight loss determination

Weight loss measurements were performed on the mild steel samples with a rectangular form of size 5.00 cm x 0.08cm x 4.00 cm in 5 M $H_2SO_4$ solutions with and without addition of different concentrations of the extract. Every sample (mild steel coupons) was weighed using a digital analytical balance and then placed in the acid solution (100ml). The duration of immersion was one hour (1hr). After immersion, the surface of the specimen (Mild steel coupon) was cleaned with distilled water using a bristled brush to scrub the surface followed by rinsing with absolute ethanol and drying with acetone. Then the sample was weighed again to calculate corrosion rates ($C_R$). This process was repeated progressively for five hours. The same experiment was carried out in the presence of ethanol extracts of *Costus afer* leaves using concentrations of 0.1 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L and 3.0 g/L at room temperature. The corrosion rates ($C_R$) of the mild steel was calculated graphically from a graph of the weight loss per surface area (mg/cm$^2$ ) was plotted against time of exposure (hrs) and the corrosion rate values obtained from the slope of the graph. The Surface coverage and Inhibition efficiency were determined using the equations below:

$$\theta = 1 - \frac{W1}{W2} \qquad \mathbf{1}$$

$$IE\% = \theta \, x \, 100 \qquad \mathbf{2}$$

where θ is surface coverage, $W_1$ is the corrosion rate of the blank solution (5 M $H_2SO_4$), $W_2$ corrosion rate of the extract and IE is the inhibition efficiency.

### 2.4. Hydrogen evolution measurements

100 mL of the corrodent (5 M $H_2SO_4$) was introduced into the two-necked flask and the initial volume of the air in the burette was noted. Thereafter, a mild steel coupon of dimension 1.20 cm x 0.08 cm x 4.00 cm already weighed was dropped into the corrodent and the flask was quickly closed. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette every minute for 30 minutes as described by Okafor *et al.* 2007. In another experiment, a set of fresh coupons were immersed in the flask containing the corrodent at different concentrations each of *Costus afer* leaves extracts (0.1 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L and 3.0 g/L). The study was conducted at 303 K, 313 K, 323 K and 333 K using a Thermostat water bath.

Each experiment was repeated twice to ensure reproducibility, and the average values were recorded.

## 3.0. RESULTS AND DISCUSSION

### 3.1. Weight loss data

The inhibitor was tested for five different concentrations (0.1 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L and 3.0 g/L) and the corresponding weight loss data are presented in Table 1. The addition of inhibitors increases the IE (Fig. 1), irrespective of the time of immersion (Singh and Anaya 2007; Okafor *et al.,* 2012). It is observed that the corrosion rates decrease, surface coverage increases and inhibition efficiency increases with increase in extracts concentration according to Xiaoyuan and Singh (2010), Ananda *et al.,* (2005), Jorge and Singh (2003) and Saratha and Meenakshi (2010). The extracts showed maximum inhibition efficiency of 93.1% at an optimum concentration of 3.0g/L. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface (Saratha *et al*, 2009; Singh *et al*, 2012; Fatemeh *et al*, 2012 and Uwah *et al.,* 2013).

**Table 1:** Calculated values of corrosion rates, surface coverage and inhibition efficiency for mild steel coupons in 5.0 M $H_2SO_4$ in the absence (blank) and presence of EECAL at 303 K.

| Variables | Blank | 0.1 g/L | 0.5 g/L | 1.0 g/L | 2.0 g/L | 3.0 g/L |
|---|---|---|---|---|---|---|
| Corrosion Rate (CR) | 74.65 | 48.17 | 41.68 | 39.08 | 14.53 | 5.17 |
| Surface Coverage (θ) | - | 0.355 | 0.442 | 0.476 | 0.805 | 0.931 |
| IE% | - | 35.5 | 44.2 | 47.6 | 80.5 | 93.1 |

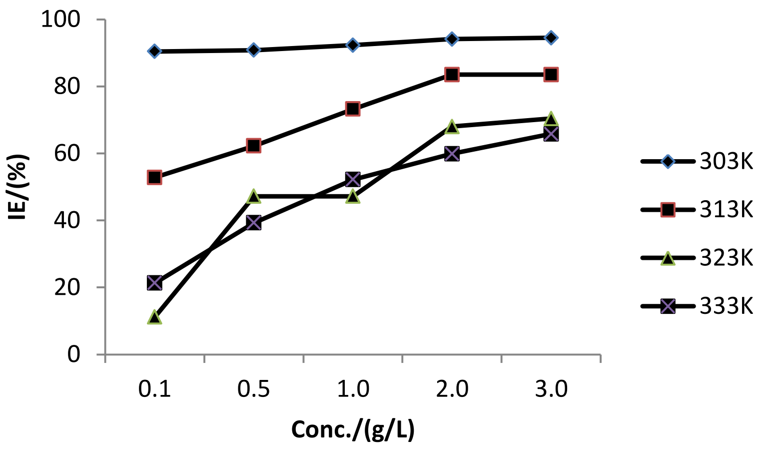

**Fig. 1:** Variation of IE (%) with concentration (g/L) of mild steel in the presence and absence of extracts of *Costus afer* in 5.0 M $H_2SO_4$ solution.

### 3.2. Hydrogen evolution data

The calculated values of rate of hydrogen evolution, surface coverage and inhibition efficiencies (%IE) for mild steel samples 5 M $H_2SO_4$ in the absence and presence of the plant extracts are presented in Table 2. From Table 2 it is observed that as the concentration of the inhibitor increases, the corrosion rate decrease at all temperatures (Fig. 2). This may be explained on the basis of the time lag between the process of adsorption and desorption according to Asher and Singh (2009) and Omar *et al*, (2009). However, the inhibitor could be effectively used at 303 K and amaximum efficiency being 93.1 %. It is obvious that variation of inhibition efficiency (%IE) with extract concentration for mild steel in 5 M $H_2SO_4$ solutions containing EECAL showed a decrease with increase in temperature (Fig. 3). The corrosion rate of hydrogen evolution however increase with increase in temperature as expected for a chemical reaction (Fig 4) . This increased Inhibition efficiency with increase extract concentration suggest that the phytochemical components of extracts are being adsorbed on the mild steel-surface, thereby reducing the surface area available for corrosion, thus inhibiting the rate of the metal dissolution process (Rehan, 2003; Raja and Sethuraman, 2008; Ananya and Singh, 2008; Bendahou *et al.*, 2006). The decrease in inhibition efficiency with increasing temperature is due to increase rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface with temperature (Singh *et al*, 2012; Saratha *et al*, 2009; Huang *et al*, 2011), and this is also in agreement with the inhibition efficiency results obtained from the weight loss values.

**Table 2:** Calculated values for rate of hydrogen evolution, surface coverage and inhibition efficiencies (%IE) for mild steel samples 5 M $H_2SO_4$ in the absence and presence of different concentrations of *Costus afer* leaves (EECAL)

| | Corrosion rate | | | | Surface coverage | | | | Inhibition efficiency (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| System | 303 K | 313 K | 323 K | 333 K | 303 K | 313 K | 323 K | 333 K | 303 K | 313 K | 323 K | 333 K |
| (Blank) | 0.119 | 0.127 | 0.125 | 0.272 | - | - | - | - | - | - | - | - |
| 0.1 g/L | 0.026 | 0.060 | 0.111 | 0.214 | 0.90 | 0.52 | 0.11 | 0.21 | 90.4 | 52.8 | 11.2 | 21.3 |
| 0.5 g/L | 0.025 | 0.048 | 0.066 | 0.165 | 0.90 | 0.62 | 0.47 | 0.39 | 90.8 | 62.2 | 47.2 | 39.3 |
| 1.0 g/L | 0.021 | 0.034 | 0.066 | 0.130 | 0.92 | 0.73 | 0.47 | 0.52 | 92.3 | 73.2 | 47.2 | 52.2 |
| 2.0 g/L | 0.016 | 0.021 | 0.040 | 0.109 | 0.94 | 0.83 | 0.68 | 0.59 | 94.1 | 83.5 | 68.0 | 59.9 |
| 3.0 g/L | 0.015 | 0.021 | 0.037 | 0.093 | 0.94 | 0.83 | 0.70 | 0.65 | 94.5 | 83.5 | 70.4 | 65.8 |

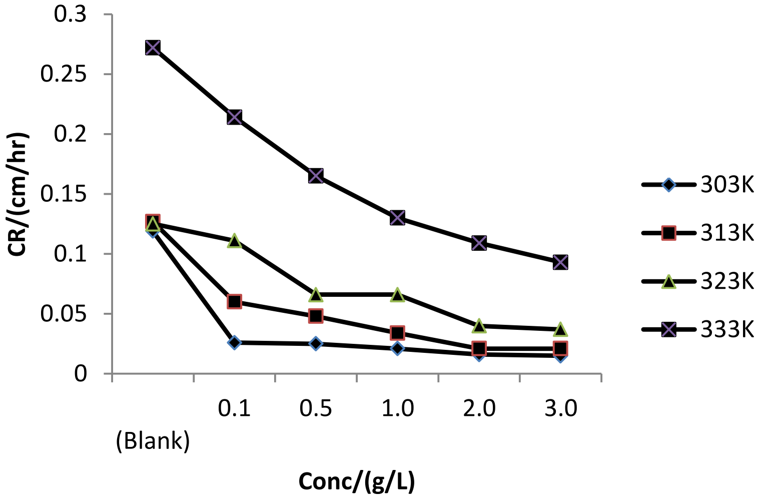

**Fig. 2:** Variation of Corrosion Rate ($C_R$) against Conc.(g/L) of mild steel in the presence absence of extracts of *Costus afer* in 5.0 M $H_2SO_4$ solution.

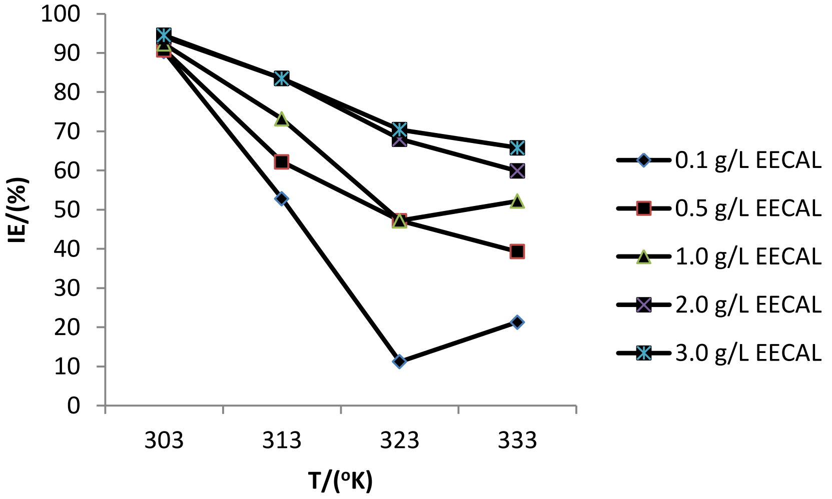

**Fig. 3:** Variation of IE (%) with temperature (K) of mild steel in in the presence and absence of extracts of *Costus afer* in 5.0 M $H_2SO_4$ solution.

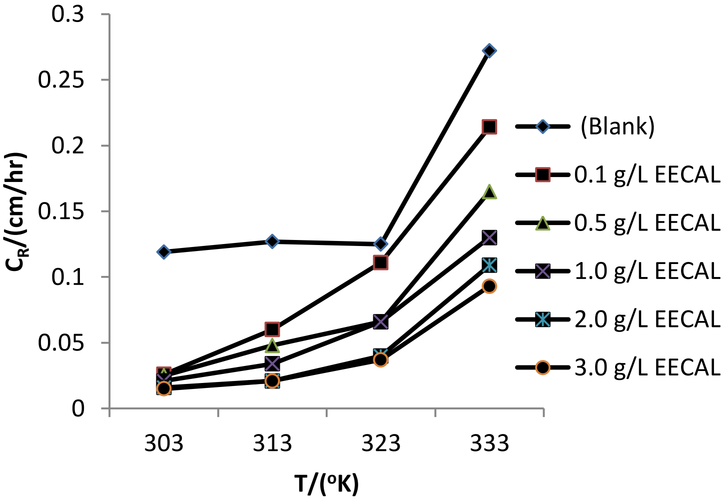

**Fig. 4:** Variation of Corrosion Rate ($C_R$) with temperature of mild steel in the presence and absence of extracts of *Costus afer* in 5.0 M $H_2SO_4$ solution.

### 3.3 Thermodynamic data

The activation energy (Ea) and other thermodynamic data, such as change in free energy of adsorption ($\Delta G^o_{ads}$), enthalpy ($\Delta H^o$), entropy ($\Delta S^o$) and heat of adsorption ($Q^*$) for mild steel in 5 M $H_2SO_4$ in the presence and absence of EECAL was calculated using equation 3 and 4; Fig. 5 and 6 and listed in Table 3. The activation energy at different concentration of the inhibitor in $H_2SO_4$ was calculated by plotting log of rate of hydrogen evolution *vs.* 1/T (Figure 5). $E_a$ values for the inhibited systems were higher than those for the uninhibited system indicating that all the inhibitors exhibited the mild steel dissolution. Low I.E were observed at elevated temperatures and this suggests a physical adsorption in the first stage (Guster and Singh, 2004; Keiser *et al.*, 2002; Camille *et al.*, 2003). This can also be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature (Guster and Singh, 2004; Patrick *et al.*, 2006a; 2006b). The range of $E_a$ is from 132.2 to 43.3 kJ/mol for EECAL in 5 M $H_2SO_4$. The negative values of $\Delta G^o_{ads}$ indicates spontaneous adsorption of inhibitors on mild steel surface. Values from -103.6 to -148.4 kJ suggest a strong interaction of the inhibitor molecules. The negative values of $\Delta H^o$ (-53.3 to -117.4 kJ/mol) indicate that the dissolution of the metal is an exothermic reaction (Okafor *et al.*, 2007; Yunqiao *et al.*, 2008; Chaieb *et al.*, 2005). This also suggests that mild steel dissolution requires more energy in 5 M $H_2SO_4$ in the presence of seed extract (Okafor *et al.*, 2012). The change in entropy (ΔS°) was found to be greater than zero (86.3 to 298.4 kJ/mol). This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible. The shift towards negative values of entropy (ΔS°) imply that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering decreases on going from reactants to the activated complex according to Okafor et al. (2012), El-Etre *et al*. (2005), Jorge and Singh, (2004) and Saratha *et al*. (2009). The negative values of $Q_{ads}$ indicate that the degree of surface coverage decrease with rise in temperature, supporting the earlier proposed physisorption mechanism for *Costus afer* leaf extracts (Asher and Singh, 2009).

$$\log\frac{CR}{T} = log\ \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad 3$$

$$Q_{ads} = 2.303\ R\ \log\ \frac{\theta 2}{1-\theta 2}\ -\ \log\ \frac{\theta 1}{1-\theta 1}\ x\ \frac{T1\ x\ T2}{T2-T1}\ kJmol^{-1} \qquad 4$$

where CR is rate of hydrogen evolution, R is the universal gas constant, N is Avogadro's constant, h is the plank constant, ΔS° is the change in entropy of activation; ΔH° and $\Delta G_{ads}$ are the changes in enthalpy and free energy of activation, θ is the surface coverage, $Q_{ads}$ is the heat of adsorbtion and T is the temperature.

**Table 3:** Values of Activation energy/thermodynamic parameters for mild steel in 5 M $H_2SO_4$ in the absence and presence of EECAL

| System | $Q_{ads}$ (kJ/mol) | Ea (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/mol) |
|---|---|---|---|---|
| (Blank) | - | 43.3 | -53.3 | -86.3 |
| 0.1 g/L + EECAL | -177.1 | 86.6 | -75.8 | -106.6 |
| 0.5 g/L + EECAL | -135.9 | 91.0 | -98.6 | -199.6 |
| 1.0 g/L + EECAL | -119.5 | 107.0 | -98.6 | -199.6 |
| 2.0 g/L + EECAL | -118.2 | 117.0 | -105.8 | -206.8 |
| 3.0 g/L + EECAL | -109.2 | 132.2 | -117.4 | -298.4 |

### 3.4. Adsorption isotherm description

Different isotherms were tested to determine its fit to experimental data (Fig 7-10). The regression values ($R^2$) obtained from these isotherms are approximately 1.0 in Table 4, showing that the data obtained for the inhibitor fits well in Langmuir, Temkin, Freundlich and Frumkin adsorption isotherms but fits better to the Langmuir adsorption isotherm (Okafor *et al.*, 2012; Fatemeh *et al*, 2012; Singh *et al*, 2007). When the regression values ($R^2$), of the fitted data are good like those obtained from this results (Fig. 7-10), it indicates that the adsorption behavior is consistent with the adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for an ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity (Saratha *et al.,* 2009; Saratha and Meenakshi, 2010). The molecular interaction parameter, 'a' obtained from Temkin adsorption isotherm is very high and hence shows attractive force existing between mild steel surface and the inhibitor. The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive property (Ananda *et al*, 2005; Patrick *et al*, 2006a).

**Table 4:** Adsorption parameters for mild steel in 5 M $H_2SO_4$ solutions containing EECAL using hydrogen evolution technique

| | Correlation factors ($R^2$) | | | | | Langmuir Isotherm | | |
|---|---|---|---|---|---|---|---|---|
| Temp. (° C) | Langmuir | Freundlich | Frumkin | Temkin | Temkin “a” | $K_{eq}$ | Slope | ΔG*ads (KJ/mol) |
| 303 K | 0.962 | 0.957 | 0.954 | 0.954 | 12.921 | 1.1025 | 0.773 | -103.6 |
| 313 K | 0.974 | 0.926 | 0.942 | 0.942 | 15.117 | 1.1792 | 0.842 | -108.8 |
| 323 K | 0.95 | 0.878 | 0.86 | 0.86 | 21.443 | 1.2488 | 0.862 | -137.8 |
| 333 K | 0.975 | 0.869 | 0.95 | 0.95 | 18.141 | 1.2953 | 1.028 | -148.4 |

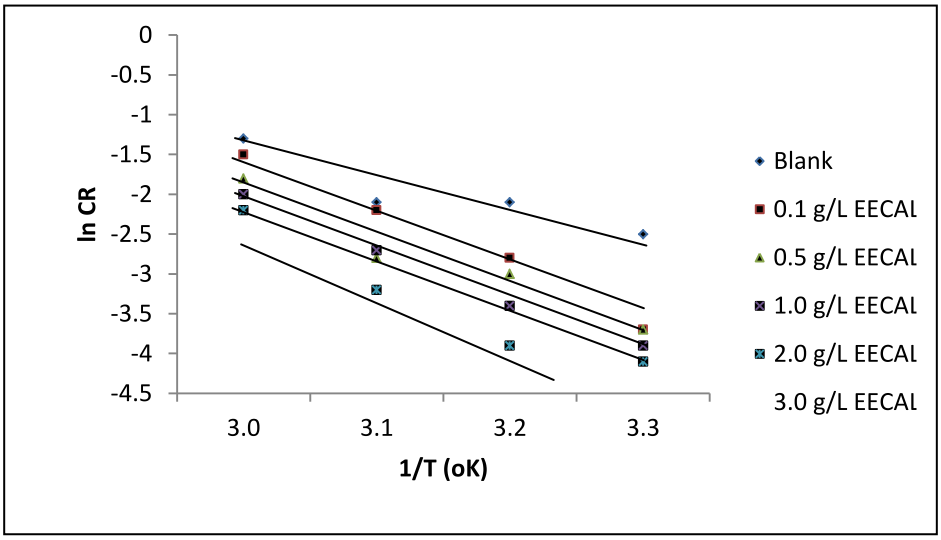

**Fig. 5:** Arrhenius plots for mild steel in 5 M $H_2SO_4$ solutions in the absence and presence of ethanol extract of *Costus afer*

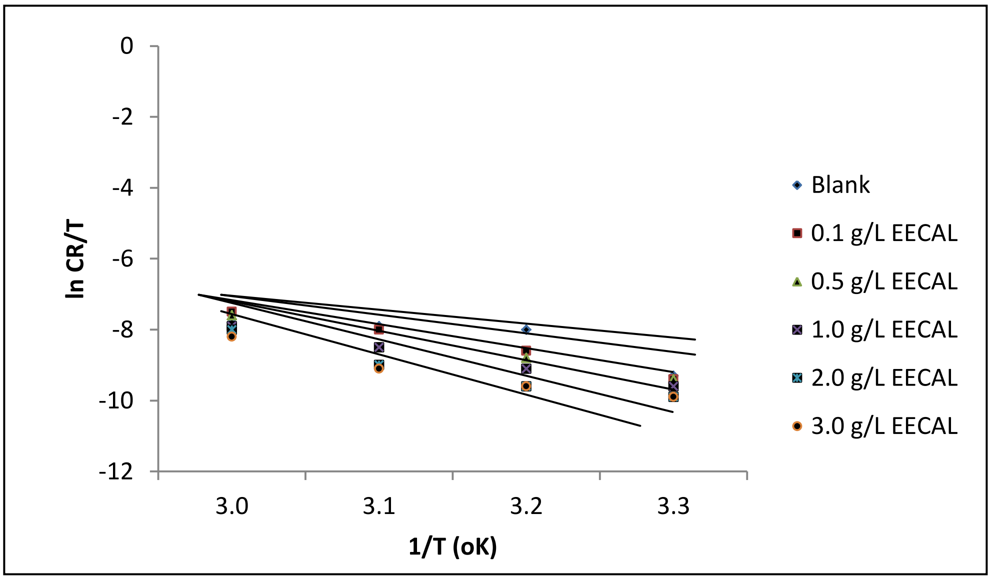

**Fig. 6:** Eyring transition state plots for mild steel in 5 M $H_2SO_4$ solutions in the absence and presence of EECAL

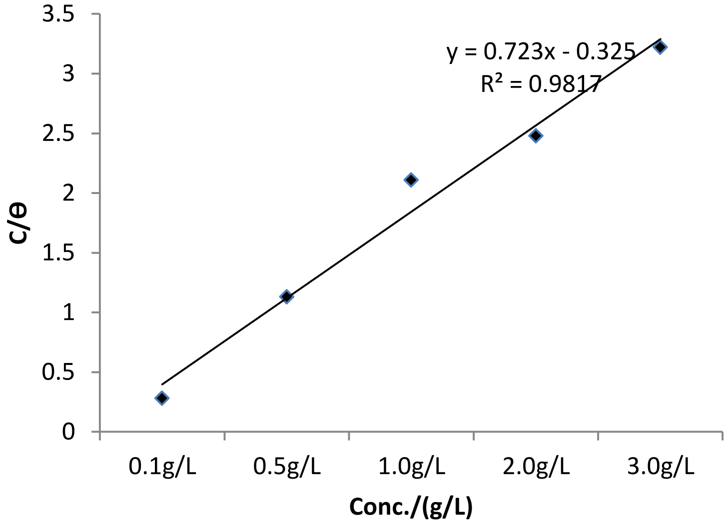

**Fig. 7:** Langmuir adsorption isotherm for mild steel samples in 5.0 M $H_2SO_4$ solutions containing ethanol extracts from EECAL

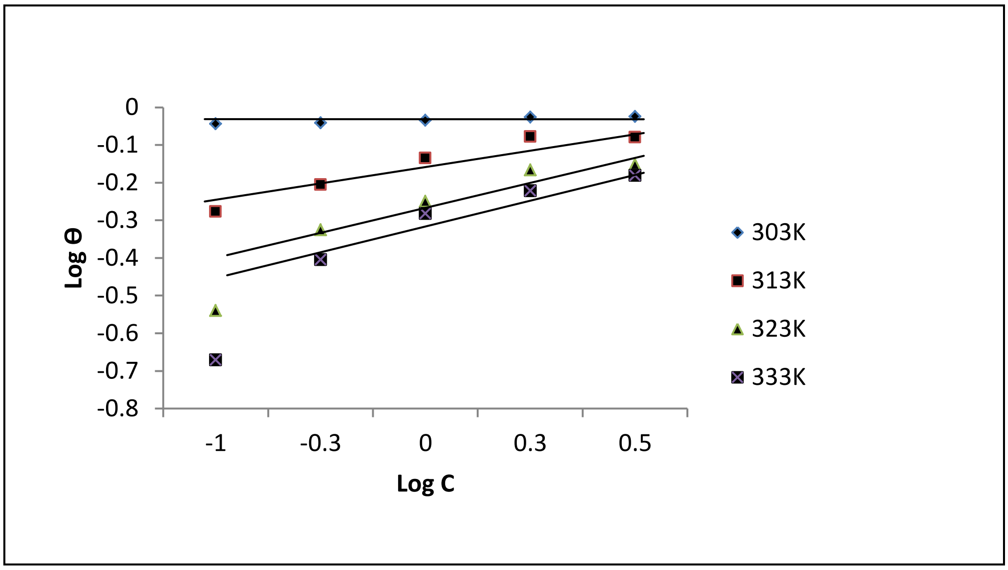

**Fig. 8:** Freunlich adsorption isotherm for mild steel samples in 5.0 M $H_2SO_4$ solutions containing ethanol extracts from EECAL

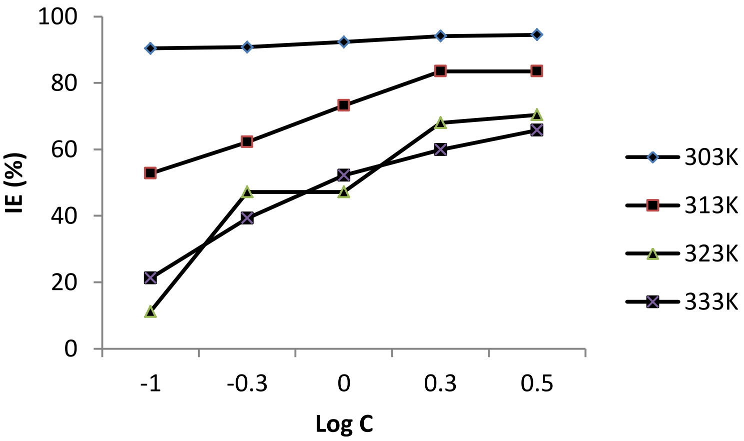

**Fig. 9:** Frumkin adsorption isotherm for mild steel samples in 5.0 M $H_2SO_4$ solutions containing ethanol extracts from EECAL

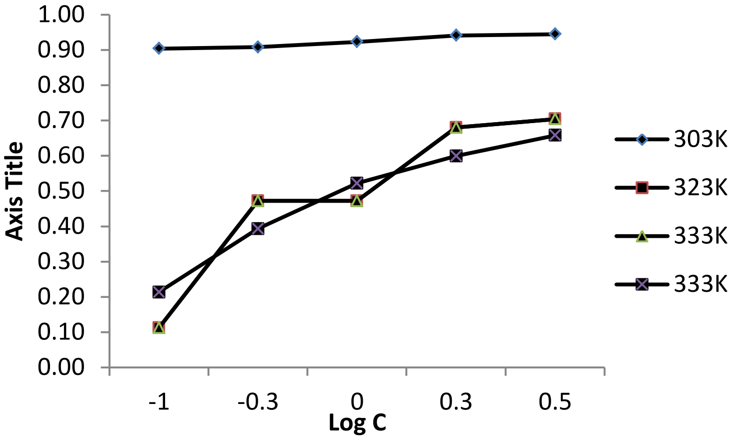

**Fig. 10:** Temkin adsorption isotherm for mild steel samples in 5.0 M $H_2SO_4$ solutions containing ethanol extracts from EECAL

## 4.0 CONCLUSIONS

1. *Costus afer* has been identified as a suitable corrosion inhibitor for mild steel in 5.0 M $H_2SO_4$ (93.1%) over a wide range of concentrations from 0.1–3.0 g/L
2. The adsorption of inhibitor on the metal surface as a spontaneous process.
3. The adsorption of active components of inhibitor obeys Langmuir, Freundlich, Frumkin and Temkin adsorption isotherms.
4. The phytochemicals present in *Costus afer* leave is physisorbed on the mild steel surface.

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