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Evaluation of the corrosion inhibition potentials of green-tip forest lily (*Clivia nobilis*) *leaves extract* on mild steel in acid media

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ABSTRACT: Plant extracts are excellent alternatives as corrosion inhibitors because of availability, low toxicity, biodegradability and low cost. In this study, corrosion tests were performed on mild steel to evaluate the effect of concentration of inhibitor, varying immersion period and temperature on the corrosion inhibition properties of *Clivia nobilis* leaves extract. This was done in H_2SO_4 and HCl acid solutions using weight loss and gasometric methods. From the weight loss results, corrosion rate and degree of surface coverage were evaluated and plotted as a function of inhibitor concentration at various immersion times. The volume of the cathodic hydrogen gas evolved was also plotted as a function of inhibitor concentration. The efficiency of inhibition in H_2SO_4 and HCl solutions were also compared. It was observed that corrosion inhibition efficiency increased with increasing concentration of *Clivia nobilis* leaf extract but not with prolonged immersion period. Experimental data obtained at 313 and 333K fitted the Freundlich and Langmuir isotherms, suggesting adsorption of *Clivia nobilis* leaves extract on the metal surface. Activation energy data described the interaction as electrostatic.

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Metal structures in use in chemical and related industries including oil and gas are exposed to aggressive substances such as acids, bases and salts containing chlorides, sulphates, nitrates, etc. (Ilayaraja *et al*., 2011). These substances have been known to accelerate corrosion particularly in processes involving acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration as iron and steel vessels or surfaces used in such processes are prone to corrosion (Marko and Fidelis, 2016). To reduce or inhibit corrosion of metals, inhibitors are employed. In the past, synthetic inhibitors such as polyethylene glycol and inorganic related inhibitors, such as those containing phosphate, chromate, and other heavy metals were widely used. However, due to the high cost and toxicity of these synthetic inhibitors, the need to find alternatives became obvious. In recent times, corrosion inhibitors of natural origin are now being preferred as they are ecofriendly, biodegradable and possess no threat to the environment (Ugi and Ageng, 2013; Devi and Rajendran, 2011; Okafor *et al*., 2007; Oguze, 2001). Several studies on the use of plant extracts for the inhibition of corrosion of mild steel have been reported (Nnenna *et al*., 2011; Patel *et al*., 2013; Obiokwu *et al*., 2015; Gusti *et al*., 2015; Fadare *et al*., 2016). Many of these authors have attributed inhibition to adsorption mechanism.

Clivia nobilis is a flowering plant of the Amaryllidoideae family. It is an evergreen long-lived plant that produces inflorescence containing between 40 and 60 pendulous flowers ranging from orange-green to red in colour. The plant has slow growth rate and takes about 6 years to flower. Clivia nobilis is commonly found in South Africa but also grows in Nigeria as well. Literature search shows that nothing is known about its medicinal values but local users have linked its ingestion to treatment of involuntary actions such as salivating, vomiting, diarrhea and paralysis.

In this research, the corrosion inhibition potential of aqueous extract of *Clivia nobilis* leaves in 2.0M H_2SO_4 and HCl solutions was investigated by evaluating the effects of inhibitor concentration, immersion time and temperature using weight loss and gasometric methods.

MATERIALS AND METHODS

Mild steel is 99.686% iron while Nickel, chromium, silicon, manganese, sulphur, phosphorus, carbon and molybdenum make up the remaining 0.314% (Ilayaraja *et al*., 2011). Mild steel specimen was pressed cut into coupons of dimensions 3.0 × 2.0 × 0.10cm, degreased in methanol, rinsed with acetone and air dried before preserving in an airtight desiccator prior to analyses (Okafor et al., 2007, Ebenso et al., 2008 and Uwah et al., 2013). 2.0M solutions of H_2SO_4 and HCl respectively were prepared. The leaves of *Clivia nobilis* were obtained from Wiiyaakara in Khana Local Government Area of Rivers State, Nigeria. The leaves were sun dried and pulverized using IS:4250 model Marlex Endura blender. The powdered samples were stored in an airtight container before use. 100g of the powder was extracted with 500ml of absolute methanol for 48 hours using the soaking method. The solution was filtered and the filtrate was concentrated with XAITD204 model NUOHAI water-bath at 60^oC until the entire methanol evaporated leaving a gel of the extract. All weighings were done using FA 2014 A Gulfex digital Scientific weighing Balance.

Weight Loss Analysis Method: Five different concentrations (0.50, 1.00, 1.50, 2.00 and 2.50g/l) of the extracted gel were prepared in 2.0 M solutions of H_2SO_4 and HCl respectively. 2.0 M solutions of H_2SO_4 and HCl without inhibitor were used as control. Seven pre-cleaned mild steel coupons were weighed separately, then each hung on a string and immersed in a beaker containing 100ml of the different inhibitor concentrations and the two pure acids without inhibitor. The inhibitor-control solutions containing the coupons were maintained at 313 K in a thermostated water bath for various time intervals (24, 48, 72, 96hrs). At the lapse of each time, the mild steel specimens were carefully washed in doubly-distilled water, dried and re-weighed. Triplicate experiments were performed for each set of the tests and the mean values reported. The procedure was repeated for temperature of 333 K.

The results obtained from weight loss (ΔW), were used to compute the rate of Corrosion (C_R), Degree of surface coverage (D_S) and Inhibition efficiency (I.E) using equations 1, 2 and 3 respectively (Obiukwu *et al.*, 2015 and Fadare *et al.*, 2016).

$$C_R = \frac{\Delta W}{At} \quad (1)$$

where ΔW is weight loss; that is, initial weight (W_i) minus final weight (W_f) of coupons, A is area of mild steel coupon (cm^2) and t, immersion time in hours.

$$D_s = 1 - \frac{\Delta W_i}{\Delta W_b} \quad (2)$$

$$IE = \left(1 - \frac{\Delta W_i}{\Delta W_b}\right) X100 \quad (3)$$

where ΔW_i and ΔW_b are weight losses in mild steel coupons with and without inhibitor respectively.

*Hydrogen Evolution Analysis (Gasometric Measurement)***:** Similarly, gasometric measurements of the corrosion inhibition process of mild steel using *Clivia nobilis* extracts in acid media were also carried out. First, 100ml of each inhibitor-acid corrodent solution was introduced into the reaction chamber connected to a burette via a delivery tube. An already weighed mild steel coupon was immersed into the reaction chamber which was immediately closed to prevent the escape of hydrogen gas. The volume (cm^3) of hydrogen gas evolved from the reaction was monitored and measured from the displacement in the level of paraffin oil in the gasometric set-up at every 60 seconds for 1800 seconds at 313 K. The procedure was repeated in the solutions containing various inhibitor concentrations (0.50, 1.00, 1.50, 2.00, 2.50 g/l). Triplicate experiments were performed for each set of the tests and the mean values reported.

The adsorption of *Clivia nobilis* leaves extract on the surface of mild steel in H_2SO_4 and HCl solutions at 313 and 333 K were analyzed using the linearized Freundlich and Langmuir isotherms (equations 4 and 5) respectively.

$$log\theta = logK_f + \frac{1}{n}logC_i \quad (4)$$

$$\frac{C_i}{\theta} = \frac{1}{K_{ads}} + C_i \quad (5)$$

In equation 4, K_f is Freundlich constant, n is adsorption intensity; K_{ads} in equation 5 is adsorption equilibrium constant while C_i and θ in both equations are inhibitor concentration and degree of surface coverage, respectively.

The activation energy of the corrosion reaction was achieved by using the Arrhenius equation

$$log\frac{C_{R2}}{C_{R1}} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (6)$$

where E_a is the activation energy for the adsorption process, C_{R1} and C_{R2} are corrosion rates at temperatures T_1 and T_2 respectively, and R is the universal gas constant.

RESULTS AND DISCUSSION

Weight Loss Studies: The average values of corrosion rates calculated from equation 1 are plotted against the different concentrations of the inhibitor in the acid media at the various time intervals and shown in Figure 1.

Figure 1 shows that the corrosion rate of mild steel was largely dependent on the concentration of the inhibitor extract in the sample solutions. As indicated in Figure 1, the corrosion rate of mild steel is greatly reduced as the concentration of clivia nobilis inhibitor increased and varies appreciably with immersion period. It is also observed in Figure 1 that at all concentrations and times, HCl reduces the rate of mild steel corrosion than H_2SO_4.

Figure 2 illustrates results of evaluated degree of surface coverage plotted against concentration of inhibitor at various immersion periods. The plots show that at lower concentrations, the degree of surface coverage is directly proportional to the concentration of the inhibitor extract and decreases at higher concentrations.

The overall results show that *Clivia nobilis* leaves extract is a good inhibitor for mild steel corrosion in both HCl and H_2SO_4 acid media. However, results suggest that the inhibitive action of clivia nobilis on mild steel was greater in HCl than in H_2SO_4 acid.

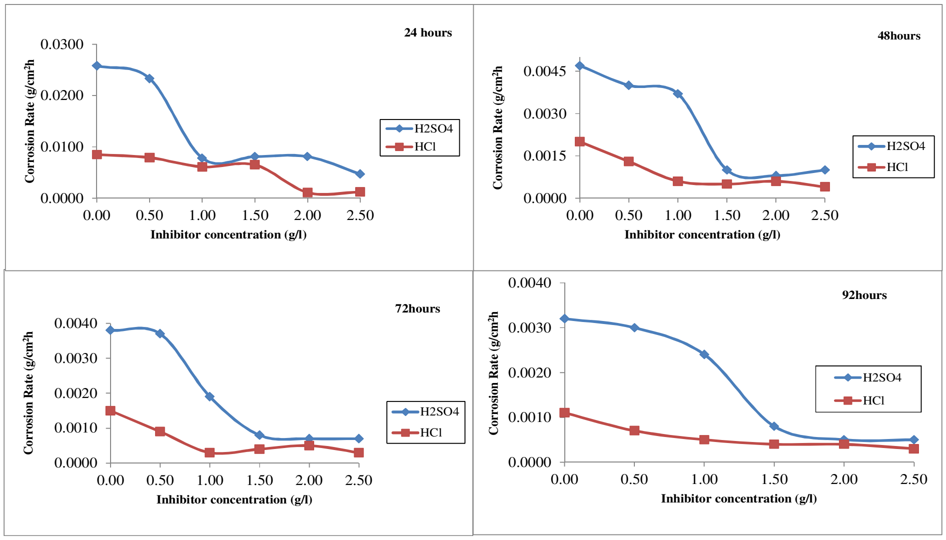

Fig 1: Plots of corrosion rate versus inhibitor concentration at various immersion times.

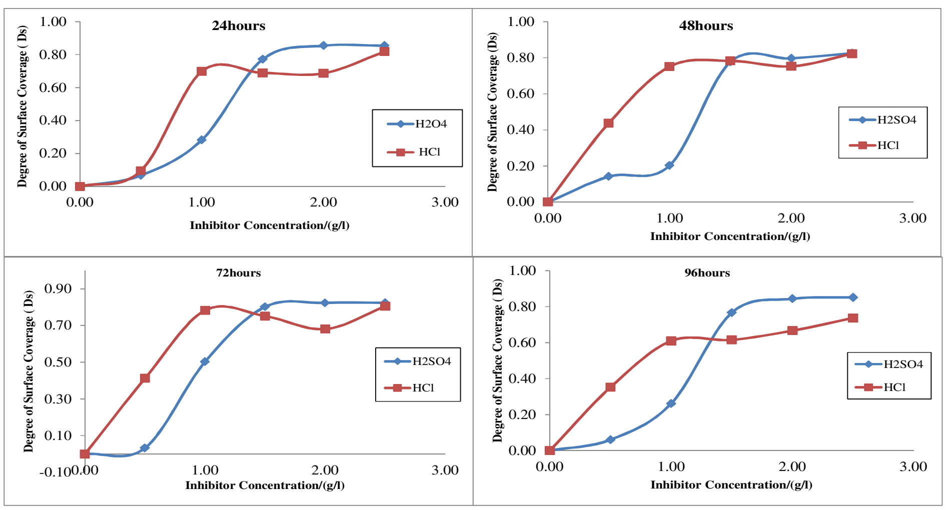

Fig 2: Graphs of degree of surface coverage versus inhibitor concentration at various immersion times.

The design of the present study did not include phytochemical screening of *Clivia nobilis* leaves extract. Nevertheless, the presence of secondary metabolites such as alkaloids, tannins, saponnins and anthraquinones, in plants extracts, containing hetero-atoms and π-electrons, have been identified to be responsible for corrosion inhibitory properties on metal surface (Fadare *et al*., 2016). Phytochemical analysis will also identify and explain the greater inhibitive properties of HCl over that of H_2SO_4.

Apparent Inhibition, Adsorption parameters and Activation Energy:

Adsorption isotherm equations (relationship between the amount of substance adsorbed and its concentration at the equilibrium solution at constant temperature) are used to describe experimental sorption data. Langmuir and Freundlich isotherms are the most widely accepted models for describing adsorption in single-solute systems, equations 4 and 5 (Sivaraj, *et al*., 2010).

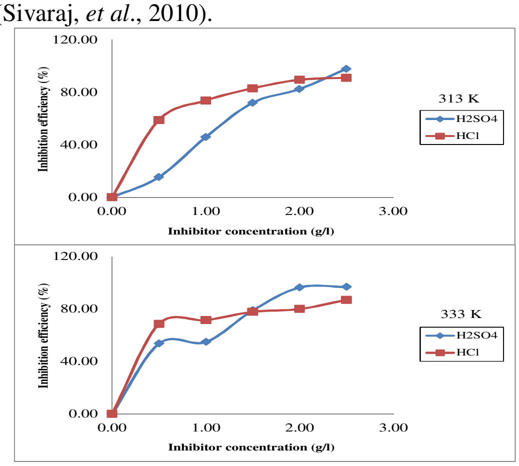

Fig 3: Inhibition efficiency of Clivia nobilis leaves extract in H_2SO_4 and HCl solutions at temperatures of 313 and 333 K.

Mild steel corrosion in absence and presence of *Clivia nobilis* leaves extract was investigated at 313 and 333 K. Results illustrated in Figure 3 show that in both solutions the corrosion inhibition potential of Clivia nobilis leaves extract on mild steel was slightly higher at 313 K than 333 K. Thus, the inhibition efficiency decreased with increase in temperature and according to Marko and Fidelis, this proves that the process is efficient at room or even low temperatures. Similar observation has also been made by other researchers (Ugi and Abeng 2013, Chetouani and Hammouti, 2003, Oguzie et al 2007 and Gunasekaran and Chauhan, 2004) who attributed the temperature effect to weak attractive forces leading to desorption on the metal surface.

Usually, the applicability of an isotherm equation is based on the best-fitting correlation coefficient (R^2). Data obtained for Langmuir and Freundlich isotherms are tabulated below (Table 1).

Table 1: Freundlich Parameters for *Clivia nobilis* extract adsorption on mild steel in H_2SO_4 and HCl solutions at 313 and 333 K.

Parameter	H_2SO_4		HCl	
Temperature (K)	313	333	313	333
K_{ads}	0.40	0.66	0.73	0.74
1/n	1.16	0.42	0.28	0.14
R^2	0.95	0.85	0.98	0.91

Table 1 illustrates that in both acid solutions, the Freundlich adsorption correlations obtained at 313 K are greater than those obtained at 333 K. This further buttresses the fact that this adsorption process is plausible.

Figure 4 shows plots of C_i/θ versus C_i of the adsorption of *Clivia nobilis* leaves extract on the surface of mild steel at 313 and 333 K, respectively. The plots at the different temperatures and acid media are linear, indicating monolayer adsorption coverage and the applicability of Langmuir adsorption isotherm to the adsorption of *Clivia nobilis* extract on mild steel, The correlation factors (R^2) for adsorption in HCl and H_2SO_4 at the different temperatures are approximately one confirming that the adsorption of *Clivia nobilis* extract on mild steel follows Langmuir process.

Figure 5 indicates that evaluated activation energies or energy barrier that has to be overcome in the presence of the inhibitor before corrosion takes place increased with increase in inhibitor concentration. This suggests that the corrosion of mild steel is much more difficult with *Clivia nobilis* and the interaction of the inhibitor extract with mild steel surface was more of physical process than chemical. Conversely, a decrease in Activation energy with increasing inhibitor concentration would have implied enhancement of corrosion and a chemisorption mechanism (Fadare *et al.*, 2016).

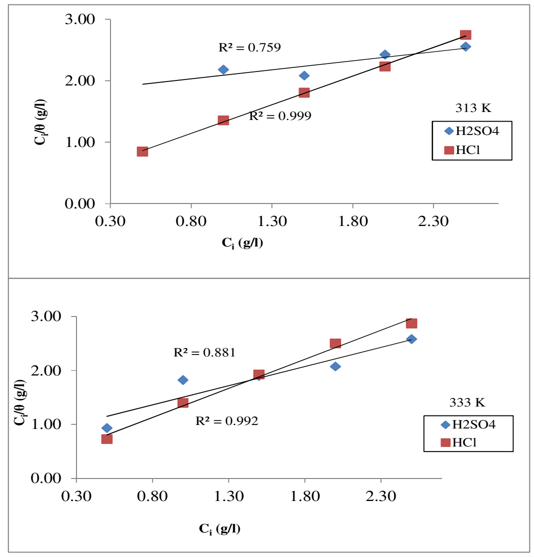

Fig 4: Langmuir isotherm for the adsorption of *Clivia nobilis* extract on mild steel in 2.0M H_2SO_4 and 2.0 M HCl at temperatures of 313 and 333 K.

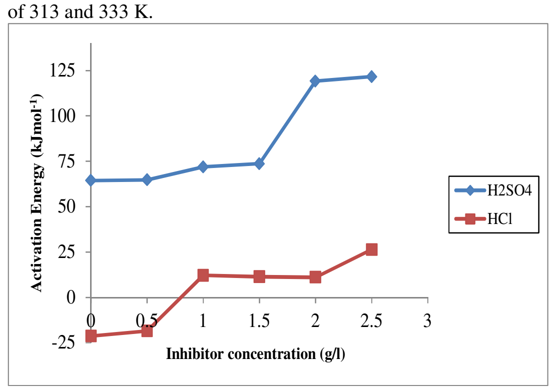

Fig 5: Plots of calculated values of Activation Energies against concentration of *Clivia nobilis* Leaves Extract.

Gasometric Studies: The rates of the anodic and cathodic reactions must be equivalent, being determined by the flow of current from anode to cathode (Negm et al., 2013). The inhibition effect of Clivia nobilis leaves extract on the flow of current from anode to cathode was monitored by measuring the volume of hydrogen gas evolved in a period of 30 minutes at intervals of 60 seconds. The results illustrated in figure 6 indicate that for both H_2SO_4 and HCl solutions, the volume of hydrogen generated at the cathode decreased with increase in concentration of *Clivia nobilis* leaves extract. This shows the inhibitive effect of *Clivia nobilis* leaves extract on the flow of current.

Conclusion Our study shows that Clivia nobilis leaves extract has corrosion inhibition ability on mild steel in H_2SO_4 and HCl solutions, with inhibition efficiency greater in HCl than in H_2SO_4 solution.

Temperature increase enhanced corrosion inhibition and inhibition mechanism was physical adsorption resulting from electrostatic interaction between the inhibitor molecules and the metal surface.

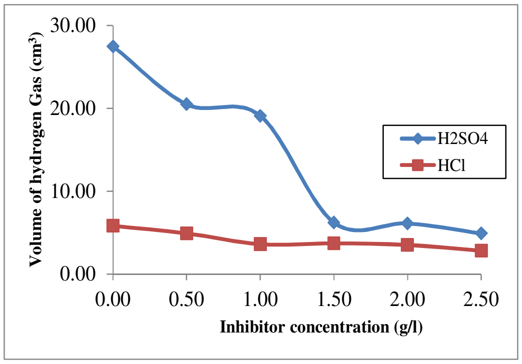

Fig 6: Volume of cathodic hydrogen gas evolved as a function of inhibitor concentration at 313 K.

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